

**A TEXTBOOK OF
GLASS TECHNOLOGY**



THE PORTLAND VASE.

[*Frontispiece.*

(*By courtesy of the Director of the British Museum.*)

A TEXTBOOK
OF
GLASS TECHNOLOGY

BY

F. W. HODKIN, B.Sc., F.I.C.

AND

A. COUSEN, M.Sc., Ph.D., A.I.C.

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FOREWORD

By PROFESSOR W. E. S. TURNER, O.B.E., D.Sc., M.Sc., F.INST.P.

BOOKS on glass technology, in the English language, dealing with the subject in its general aspects, are singularly few. Apart from books on stained glass and those intended for glass collectors, it would be difficult to name half a dozen books issued during the last one hundred years in this country which have been of general service to the glass manufacturer or glass worker. One of the tools which we found non-existent when, in 1915, we set up teaching courses in the department of glass technology, was a textbook. The small but, in its day, excellent introduction to the subject by Messrs. Powell, Chance, and Harris, published in 1883, had long been out of print and out of date and there were available only two books in English; but these did not profess to give more than a general popular account of the manufacture of glass.

The textbook to which I have the pleasure of writing this Foreword has been a long time in making its appearance. It was undertaken in 1916, but the many and varied demands of a rapidly developing industry rendered it impossible to find the necessary time for its compilation. Messrs. Hodkin and Cousen finally undertook to prepare the book. Both are experienced teachers; both have acquired considerable knowledge of the experimental melting of a wide range of glasses, and one of them has frequently had to deal with works problems. I should like to congratulate them on a very creditable piece of work. They have spared no effort to obtain material to make the book both accurate and up-to-date; and, in my opinion, as a general account of the underlying principles of glass technology, it will bear very favourably a comparison with any book previously issued in any language.

The appearance of the textbook will, I know, fill a long-felt want. It will, I trust, do more. Those manufacturers who have not perhaps previously realised it may, from perusal of the book, get a clearer idea of the breadth of the subject of glass technology and the necessity for a knowledge of the fundamental principles of the various sciences which all go to the making of the subject. They will, I trust, more and more feel it incumbent on them to see that their sons who may succeed them, and other persons who may occupy responsible positions in the factory, shall at least know their job thoroughly from the technical point of view.

During the past nine years, the department from which this is written has not only trained students at the university, but has also initiated and subsequently supervised classes in the elements of glass technology in centres all over Great Britain. We have discovered from actual contact with them that amongst the workers in the industry there is a

considerable number seeking precise knowledge of the principles of glass-making; and, given encouragement, the number who are thus interested in their work could be increased. In some centres of the industry their number has been too few to make the formation of a class possible; or, in some cases, the lack of a skilled instructor has been a handicap. The appearance of this textbook makes possible serious study of the subject amongst those who are thus isolated. To those manufacturers and managers on whom the problem of labour often presses hardly I would like to suggest that there are everywhere workmen whom it would repay to encourage as serious students; and that such students should always be first considered for promotion when higher positions become vacant.

The success of the glass industry must depend in an increasing degree on the thoroughness of the technical knowledge of its leaders, and this introductory textbook of Messrs. Hodkin and Cousen is, I believe, a definite and helpful contribution to this end.

DEPARTMENT OF GLASS TECHNOLOGY,
UNIVERSITY OF SHEFFIELD.
July 4, 1924.

PREFACE

THE present volume represents, we believe, the first systematic attempt in the English language to treat of the technology of the glass industry. As the work progressed it became increasingly evident that the greatest difficulty confronting the authors lay in deciding as to the extent to which each section of the subject should be elaborated. It will be evident that a detailed treatment of the history, of the underlying theory, and of the practice of the individual branches of the industry, in a manner sufficiently clear to be grasped by the general reader, and yet concisely enough to keep the book within reasonable bulk, is a problem not easily solved. No attempt has been made, therefore, to make the succeeding pages an encyclopædic survey, but they have been allowed to take the simpler form of a general introduction to the subject.

Technological books often become mere compilations of patent specifications and manufacturers' catalogues, a fault which we have striven to avoid. In the case of the more complicated furnaces or machines a general description only has been given, for details of construction (best grasped by practical inspection) tend to obscure statements of general principles which we are most desirous of teaching.

Methods of carrying out many of the processes here described vary from factory to factory, whilst Continental and American methods also often differ profoundly from those employed in this country. Since it would be impossible to describe all the variations likely to be found, average processes have been considered, and where the procedure in other countries appears to be better than that in England, the foreign methods have been given preference.

Since the keynote of the volume has been simplicity, theories at present in debate have been treated only lightly, and the more complex side of them often passed over. In this respect we may cite the speculations as to the nature of glass. The "colloidal theory," although it has many adherents, is not yet definitely proved, and an explanation of it has been considered to be out of the scope of the present work. In the practical sphere, for the same reason, optical methods of measuring strain, such as have been worked out in the German optical glass factories, have been passed over as being too complex for the average manufacturer to put into practice.

In conclusion, we believe that this volume will meet a long-felt desire, and that it will be of use to all ranks of those engaged in the production of glassware, to masters who desire factories run on sound and up-to-date principles, and to workmen who wish to know something of the theory involved in the processes in which they are day by day engaged.

F. W. H.
A. C.

DEPARTMENT OF GLASS TECHNOLOGY,
UNIVERSITY OF SHEFFIELD.

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American Journal of Science	<i>Amer. J. Sci.</i>	New Haven, Conn., U.S.A.
Annalen der Physik.	<i>Ann. d. Phys.</i>	Leipzig.
Annalen der Physik (und Chemie)	<i>Ann. Phys. Chem.</i>	Halle.
Annales de Chimie et de Physique	<i>Ann. Chim. Phys.</i>	Paris.
Annales des Mines	—	Paris.
Berichte der Deutschen Chemischen Gesellschaft	<i>Ber.</i>	Leipzig.
Bulletin of the American Institute of Mining Engineers	<i>Bull. Amer. Inst. Min. Eng.</i>	Philadelphia.
Bulletin de la Société de l'Industrie des Mines	<i>Bull. Soc. de l'Ind. Min.</i>	—
British Clayworker	<i>Brit. Clayworker</i>	London.
Chemical News	<i>Chem. News</i>	London.
Comptes rendus hebdomadaires des Séances de l'Académie des Sciences	<i>Compt. Rend.</i>	Paris.
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Chemisch Weekblad	<i>Chem. Weekblad</i>	Amsterdam.
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Engineering	—	London.
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Die Glashütte	—	Dresden.
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Journal of the American Ceramic Society	<i>J. Amer. Cer. Soc.</i>	Easton, Pa., U.S.A.
Journal of the American Chemical Society.	<i>J. Amer. Chem. Soc.</i>	Washington.
Journal of Industrial and Engineering Chemistry	<i>J. Ind. Eng. Chem.</i>	Washington.
Journal of the Optical Society of America	<i>J. Opt. Soc. Amer.</i>	Rochester, N.Y.
Journal de Pharmacie et de Chimie	<i>J. Pharm. Chim.</i>	Paris.
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Pottery Gazette	—	London.
Proceedings of the Institute of Cleveland Engineers	<i>Proc. Inst. Cleveland Eng.</i>	—
Proceedings of the Institute of Mechanical Engineers	<i>Proc. Inst. Mech. Eng.</i>	London.
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Zeitschrift für analytische Chemie	<i>Zeitsch. anal. Chem.</i>	München.
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A TEXTBOOK OF GLASS TECHNOLOGY

CHAPTER I HISTORICAL

PART I.—TO THE BEGINNING OF THE NINETEENTH CENTURY.

(1) **Egyptian.**—The oldest record of the manufacture of glass that can be relied upon with certainty comes from Egypt. Beads adorning some of the mummies there discovered are coated with a coloured glaze, which is a true glass, whilst amongst the tombs of Thebes, pieces of blue glass, similar in composition to the glaze upon the beads, have been found. According to Flinders Petrie, glass-making in ancient Egypt, as distinct from the glazing of pottery, dates back not further than 1600 B.C., and the method then employed was to shape the glass around a core of sand. It was not until many centuries later that ware was made from blown glass. The glass-houses of Alexandria were long famed for their ware, and Egyptian glass was carried abroad by the trading Phœnicians, who also probably learned the art of its manufacture from this source.

(2) **Roman.**—Rome was, at one time, supplied with much glass from Alexandria, the trade assuming large proportions in the first century B.C. About this period many Egyptian workmen were attracted to Rome, and a number of factories were founded there. The manufacture of rude drinking vessels was carried out from the time of Nero (A.D. 54-68), but the art of glass-making, at first, made slow progress amongst the Romans. A century or so later, however, the manufacture and decoration of glass assumed such proportions that in A.D. 220 Alexander Severus laid a tax upon the glass manufacturers of Rome, who existed in such numbers at this time that a principal quarter of the city was assigned to them for the prosecution of their calling. The Portland vase (see frontispiece), which is composed of a deep blue glass, ornamented with white opaque figures in bas-relief, sculptured in the form of cameos, belongs to this period. Lactantius at the close of the third century A.D. first noted the use of window glass, whilst at a later date (422) we are told by St. Jerome that glass melted and cast into plates was used for windows, and Paulus Silentarius, a hundred years later still, observed the same use for glass in Constantinople. In the Roman provinces of Gaul and Britain, during the period of occupation, the manufacture of articles of glass was undoubtedly carried out.

(3) **Venetian.**—Amongst mediæval nations, the Venetians, who commenced the manufacture in the thirteenth century, were famed for their glassware. In particular, they excelled in the creation of mirrors and

of drinking glasses. Venetian glassware was singularly beautiful in form, and decorated in many ways, as with colours, gilding, filigree work, etc. It is interesting to note that Venice possessed the secret of making *aventurine* glass, an art which was afterwards lost. The industry was chiefly carried on in the neighbouring island of Murano, and reached its greatest heights in the sixteenth and seventeenth centuries. It was so important that members of the Corporation of Glass-makers held a privileged position in the State, whilst heavy penalties were inflicted upon those who went abroad and taught the art to foreigners.

(4) **French.**—Early in the fourteenth century France attempted to foster the art by rendering the manufacture of glass profitable to its aristocracy, but it was long before French products rivalled those of Venice. Under the ministry of Colbert, some French subjects, who had learned at Murano the method of making sheet glass, returned to France, and in 1665 were established by the minister near Cherbourg. In 1688, Thévert of Paris, and later of St. Gobain, invented the art of casting glass plates, and was able to produce sheets of a size 84 × 50 inches; no sheets made by blowing ever exceeding 50 inches in length. The two rival French companies, after much quarrelling, amalgamated in 1695, and were later very successful under the direction of A. d'Agincourt.

(5) **English.**—In England, Bede states that in 674 the Abbot Benedict sent for foreign workmen to glaze the windows of the church and monastery of Wearmouth in Durham, these men being our first instructors in the art of making window glass. Even in the eleventh century, however, glazed windows were not at all common in England, and as late as the thirteenth and fourteenth centuries few ordinary houses were so provided, although in France and Italy glass had been widely used for windows at a much earlier period. There is a reference to the manufacture of glass in 1439 by the Countess of Warwick, in which it is stipulated that English glass should not be used in the windows of the Beauchamp Chapel at Warwick. During the reign of Elizabeth the manufacture of glass was fostered by the State, though with but indifferent results. At this period a discovery was made which, in the course of time, largely revolutionised the whole industry, and served, more than anything else, to undermine the pre-eminence of Venice. It was the discovery of lead flint glass, stated to have been first made in London in the year 1557 at Savoy House in the Strand and in Crutched Friars, although its origin is in doubt. Covered pots for melting the glass were also an English invention of about this period. Almost eighty years later—namely, in 1635—Sir R. Mansell obtained a monopoly for the manufacture of flint glass, the reason being that he employed pit coal instead of wood for his furnaces. That Venetian glass at this time was still highly valued is shown by the fact that Mansell's business partially consisted in importing such ware, and it was not until about fifty years later that the country became independent of Venice for fine quality drinking-glasses. Credit for the improvement of English products belongs largely to the second Duke of Buckingham, who brought Venetian artists to London in 1670 for the manufacture, first of drinking ware, later of sheet glass. With the improvement in quality of the articles manufactured, English lead or "crystal" glass, which lent itself so admirably to the production of high

lustre and brilliancy when decorated by cutting, proved to have a greater attractiveness than the lime glass made in Venice. From this time the fate of the Italian industry was sealed, and as the seventeenth century drew to a close, Venetian glass was imported in diminishing quantities.

Although London was the first centre of the English glass industry, it was soon followed by Newcastle-upon-Tyne, where Mansell finally settled, Stourbridge, Bristol, and other districts. Houghton, in 1696, gave a list of the glass-houses of England and Wales, from which it appears that they totalled about ninety, thirty-eight making bottles; two, looking-glass plates; five, crown glass and plates; six, window glass; and nineteen, flint, green, and ordinary glass. To instance the variety of articles made by some of the old factories we may quote a list of those manufactured at Bolsterstone* (see Fig. 1), a South Yorkshire factory founded in the seventeenth and flourishing throughout this and the following century. The list includes crown glass of good quality for windows; bottles of varying sizes and shapes and for many purposes, domestic and commercial; also fancy articles, such as basins, buttons, bells, bellows, butter pots, candlesticks, comfit glasses, cream jugs, dolls' glassware, firing glasses, ink bottles, knife rests, mustard bottles, punch fillers, pepper bottles, porringers, scent jars, spoons, sweetmeat glasses, thumb glasses, toddy lifters, salt cellars, tobacco pipes, vinegar bottles, walking sticks, and weather glasses. It is truly a formidable list, and speaks volumes for the energy and adaptability of the manufacturers of glass in England during this period. The first large English factory for the production of cast plate glass was established in 1773, near Prescott in Lancashire.

(6) **Irish.**—Towards the end of the eighteenth century cut glass-ware was manufactured in Ireland, particularly in and around Waterford. The "Waterford" glass is characterised by a faint, but quite distinct, blue tint caused by the presence of a trace of cobalt. In addition to ordinary heavy cut glass in the form of chandeliers, candelabra, decanters, fruit and butter dishes, some decorated ware was produced, the process most frequently adopted being that of gilding. The metal was "burned" into the glass by means of a flux, usually borax.

(7) **German and Bohemian.**—The time when glass was first made in Germany is uncertain, although Tscheuschner adduces as evidence that painted windows of glass were used in a Bavarian church in the tenth century. In general, unlike those in England and France, the first German glass-works were small factories set in the heart of the forest, where wood fuel and potash were plentiful and cheap. Bohemia was the first home of the industry, records being available to show of the erection of factories in the Haida-Steinschönau districts in the fifteenth and sixteenth centuries. From Bohemia glass-making spread, in the course of time, to the neighbouring region of Thuringia. In the Steinschönau district, in 1694, a number of articles were manufactured, including plate and hollow-ware, whilst Count Kinsky (1722-80) erected at Burgstein a mirror factory and at Swoika a glass bead works. So important had the Bohemian industry become in the middle of the eighteenth century that efforts were made, as in Venice at an earlier date, to prevent it from spreading abroad.

* J. Kenworthy, *J. Soc. Glass Tech.*, 1918, 2, 5.

At the close of the century, times of great difficulty occurred, caused by the destruction of the Napoleonic wars, and by English and French competition. The troublous times were successfully negotiated, however,

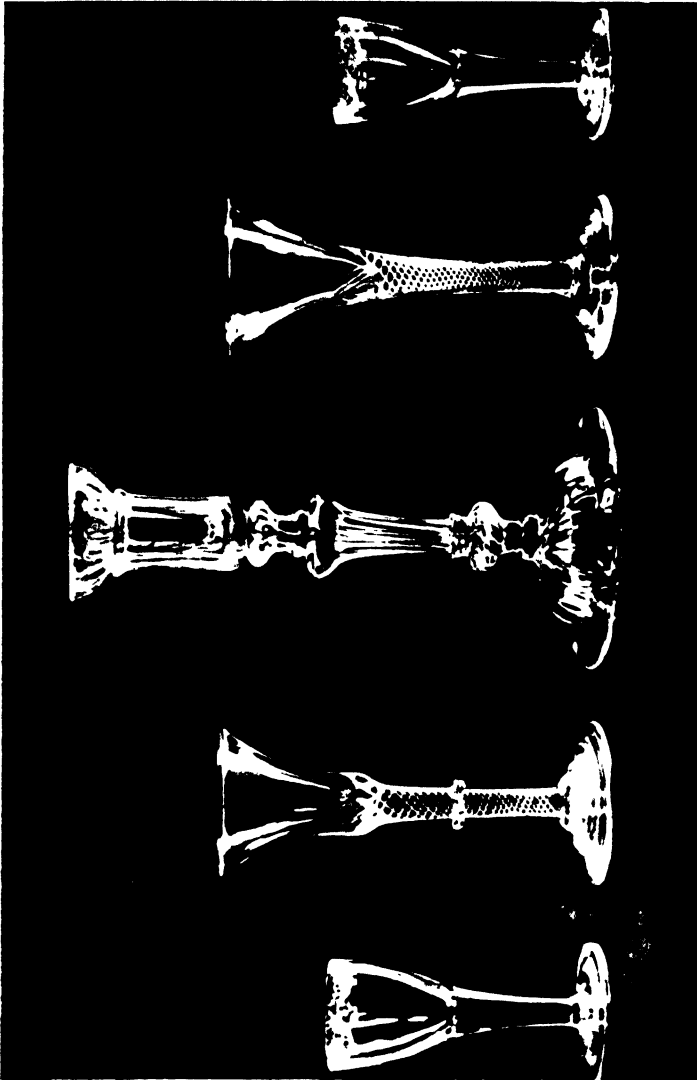


FIG. 1.—CANDLESTICK AND DRINKING-GLASSES MADE AT BOLSTERSTONE GLASS HOUSE, A.D. 1700-1740
(By courtesy of J. W. Kenworthy, Esq., Deepcar, Sheffield.)

and once again Bohemia assumed a commanding position amongst the glass manufacturing districts of the world.

(8) **American.**—Turning now to America, we find that the first important glassworks was erected in 1790 in New Hampshire, by Robert Hewes, for the production of window glass. His venture proved a failure,

and the industry languished until the early years of the nineteenth century. About this time the production of window glass and of bottles, generally made in the same factory, was successfully undertaken, and it became a permanent industry in the country.

PART II.—RECENT PROGRESS.

We shall, at this point, endeavour to envisage the methods employed at the close of the eighteenth century, and from thence trace their advancement, individually, to the present time.

(9) **Materials.**—By far the greatest bulk of glass manufactured was of the alkali-lime-silica variety. Two methods of obtaining the alkali were in use. In some districts, close to forests, wood was burned, the ashes lixiviated with water, and, by recrystallisation, a crude potash was obtained. Other factories, near to the sea, employed the ash of seaweed, purified also by lixiviation, and consisting chiefly of soda (sodium carbonate). As the industry grew, potash was largely replaced by soda from seaweed, of which Spain became a large producer and exporter. It was during the Napoleonic wars, when the blockade prevented France from obtaining supplies of soda, that Leblanc, in 1806, devised the method which bears his name, of producing salt-cake and soda-ash. The large supplies of sodium chloride everywhere available, both as rock salt and brine, at once assured success to the new method. Rivalry between salt-cake and soda-ash has continued throughout the past century, being conditioned by prices, by the types of furnace employed, and by individual predilections of the manufacturers. The advent of the Solvay process for making soda-ash in 1863 has largely turned the scale in favour of that product, although, as we shall see later, the admixture of some salt-cake is even now found necessary. Of recent years, wood ash as a source of potash has been largely displaced by the large deposits of potassium salts found at Stassfurt in Germany. Of other materials employed a hundred years ago, sand and limestone or chalk are still used, the only change being the tendency to use purer, more iron-free samples, for the production of a glass of better colour. The use of ground flints as a source of silica has long been discontinued, and "*flint glass*" is no longer so denoted because of the origin of its silica. In some districts, particularly in America, the use of fairly soft, easily crushed sandstones has been largely followed. In general, the quality of all batch materials, particularly manufactured ones, has tended to improve with the improvement of chemical processes, and in some cases natural products have been ousted by more reliable, chemically prepared substances. For example, bone ash, as an opaliser, is now very largely replaced by calcium phosphate, of the same composition but of much greater purity. We may note the introduction in recent years of selenium as a colouring agent and decolouriser; also of the application of boric acid, borax, and a number of other compounds for glasses required for special purposes.

(10) **Furnaces.**—At the commencement of the nineteenth century glass was universally melted in pots, set in a furnace and directly heated, generally by a centrally placed fire, burning wood or, sometimes, coal.

About 1850, wood was largely replaced by coal as a fuel, though even to-day some factories burn wood. A great revolution in furnace construction followed the introduction by F. and W. Siemens, about 1860, of heating by means of producer gas and the regenerative preheating of air and gas. Another important step was the introduction by F. Siemens of Dresden, in 1872, of the tank furnace. In recent years recuperation has, to some extent, replaced regenerative heating for pot furnaces. For the annealing of glassware, kilns were largely employed, although lehrs, in which the goods are slowly passed on trays down a tunnel heated at the front, have been in use for more than a hundred years. Of modern types of lehrs the chief innovations are "*muffle*" lehrs, in which the heating gases are burned in a separate chamber and do not come into contact with the glass, and electrically heated lehrs.

(11) **Bottle-Making.**—In the early years of the nineteenth century two methods of making bottles were employed. The first consisted of shaping the bottle on the *pipe* and *pontil* entirely with tools. The second method was that in which an open mould was used. The mould was made of clay or of metal, was open at the top, and shaped the bottle up to the shoulder, leaving the neck to be fashioned by the skill of the workman during the process of blowing. Since it did not allow of the production of bottles uniform in size, the use of open moulds was replaced, first in Germany, then in other countries, by the use of closed moulds. In the latter, the neck itself was shaped as well as the body of the bottle, and uniformity of size was assured. With the closed mould came the use of the marvering block, a table of stone or iron for shaping the "*parison*"* before placing it in the mould. To obviate the considerable effort required in turning the glass in the mould during the blowing period, a method necessary when the vessel was required to have a smooth and even external surface, Cahuc of Dorignies (France) in 1878 devised a revolving mould, thus allowing the workman to hold his glass stationary.

The first successful bottle-blowing machine was devised by Ashley of Castleford (England) in 1888, after sundry attempts by other workers, and it was followed, in the next few years, by machines by many makers in Europe and America, notably those by Dobson, Beckett, Spaull, Hilde, Grote, Heerdt, Severin, and Boucher. All the above were semi-automatic, and required the assistance of a gatherer. In recent years America has led the field in regard to bottle machines, and semi-automatic machines devised by O'Neill, Lynch, E. Miller, W. J. Miller, Cox, and Graham are at the present time very largely used. In addition, the completely automatic Owens machine is an American invention. To displace the human element in the semi-automatic machine, feeding devices for the supply of glass to the moulds have been introduced. The first such device was patented by Homer Brooke of New York in 1901, and it has been followed by many others, some of which will be described later.

(12) **Window and Plate Glass.**—Although, as we have seen, some of the window glass used in the eighteenth century was of cast plate, the great bulk in actual use was "*crown*" glass, made by blowing on

* From the French "*paraison*."

the pipe, a process centuries old. By it, a gathering of glass, usually weighing 10 or 11 pounds, was, by marvering and blowing, worked into a globe of suitable size. The portion of the globe furthest removed from the pipe was flattened somewhat, and a *pontil* (or "*puntty*") attached to it. By cracking off the pipe a circular hole was left in the glass about 2 inches in diameter. On reheating the globe, and spinning it with a sufficient velocity, the hole was rapidly enlarged. Ultimately a circular sheet, 50 to 60 inches in diameter, was produced, having a uniform thickness except at the point where the pontil was attached, at which point was a lump called the "bull's eye."

During the century the method at present used, that of blowing cylinders, and afterwards cracking them open and flattening them into sheets in special ovens, was introduced. According to Henrivaux it was first practised in France by Czech workmen brought by Drolinvaux and settled at Saint-Quirin. Since its introduction, the "cylinder" process has been modified in several ways. In many factories the flattening ovens are heated by coal gas, whilst Biévez ovens have replaced the old fixed type. Lippert of Bohemia, in 1825, replaced the wooden flattening apparatus by one of refractory material.

The first attempt to draw glass in sheet form was made by William Clark of Pittsburg, U.S.A., whose process was patented in 1857. The method did not prove satisfactory, nor did those which immediately succeeded it, since the tendency of the molten sheet to contract in breadth as it was drawn could not be overcome. It was not until 1902 that the difficulty was overcome; in that year E. Fourcault of Lodelinsard (Belgium) patented a sheet window drawing machine of a type now coming into widespread use. Very shortly afterwards (1905), I. W. Colburn of Franklin (Pennsylvania), who commenced his researches in 1900, patented a machine for drawing glass continuously in sheets, but the method has only proved commercially successful since 1918 under the ægis of the Libbey-Owens Company. The improved Colburn machine in 1923 made about 25 per cent. of the window glass of the United States. The solution of the problem along other lines was effected by J. H. Lubbers of Pittsburg, who commenced to study the problem in 1894, but was only successful on a commercial scale in 1904. Lubbers' method consisted of blowing mechanically, on a large scale, cylinders of glass (up to 40 feet in length) from a reservoir of molten metal.

Plate glass was made at St. Gobain in France, and in England, during the eighteenth century, by rolling out the molten metal on a copper plate or table by means of a copper cylinder. After several disasters through the cracking of the table the English firm replaced it by one of iron, with successful results. In essentials the method then adopted is the one now employed, the principal changes being those in the method of annealing, of grinding, and of polishing the plate. It was not until 1879 that plate glass was successfully produced in the United States, after years of fruitless effort. Up to about the year 1900, kilns were employed for annealing the sheets, but, at the present time, mechanically operated rod-lehrs have replaced the old kiln annealing ovens. In the old process, grinding was done on rectangular tables moving with a reciprocal motion.

the grinding tool having a motion at right angles to that of the table. To-day the grinding instrument consists of a large, rotating, circular table, having special grinding tools, for details of which the reader is referred to the chapter on plate glass.

In conclusion we may mention the production of wired glass by F. Shuman of Philadelphia in 1892, and of heat-intercepting structural glass, made commercially possible by the work of L. T. Sherwood during the last few years.

(13) **Pressed Glass.**—Of recent years much thick-walled hollow-ware has been made by pressing in moulds, for which special machines have been designed. For this purpose soda-lime and potash-lime glass has largely ousted the expensive lead glass, whilst still more recently alkali-barium glasses, owing to their great suitability for pressed ware, have enjoyed a wide popularity.

(14) **Optical Glass.**—There is little to chronicle of the development of optical glass until the latter years of the eighteenth century. At that time the range of optical *crowns* and *flints* was very restricted, and the chief efforts of workers lay in improving technical manipulation, and in extending the *dense flint* series of glasses. The greatest problem of all, the production of glasses giving achromatic combination, remained untouched. Fraunhofer of Munich, who along with Guinand of Neuchâtel had done much to improve the technical side of the subject, also studied spectrometrically seven glasses, and actually found a pair which practically destroyed chromatic aberration. He did not attempt, however, to produce the glasses on a commercial scale. Up to this time it was only possible to obtain lenses up to three or three and a half inches in diameter without striæ; but in 1790 Guinand first produced some of a diameter as great as nine inches. His method, for long kept profoundly secret, consisted in mechanically stirring the glass with a fireclay rod. This worker, after joining Fraunhofer and Utzschneider at Munich, carried on the successful manufacture of optical glass.

One of the sons of Guinand, preserving his father's secret, joined Bontemps at Choisy-le-Roi without there achieving success. Bontemps himself, however, persevered and was able in 1828 to produce homogeneous discs up to fourteen inches in diameter. In 1848 Bontemps joined Messrs. Chance Bros. of Birmingham, who thereupon became the most important firm of lens glass manufacturers. At Paris, Feil, a grandson of Guinand, continued the production of optical glass, and the interests of the firm he created have now passed down to the modern firm of Messrs. Parra-Mantois of that city. Of some interest to the optical industry were the researches of Harcourt, an English clergyman, carried out between 1834 and 1859. This worker systematically examined a large number of new types of glass. His work was performed in the form of small meltings in a crucible rotated by clockwork and revolving within a spiral burner using hydrogen as fuel. Unfortunately the glass was not stirred, and accurate comparative optical measurements could not be obtained. In 1862, Harcourt was joined by Stokes, but although a large amount of fundamental knowledge was collected, practical results were only few. As a matter of fact Harcourt actually made, in the course of his researches, a triple objective from two borate glasses and a *crown*

disc, and so fully proved the possibility of producing a combination free from secondary spectrum.

In 1878, Abbe published a paper in which he dealt with the improvements necessary in optical glasses in order to secure an advance in the performance of refracting instruments. Abbe's paper held the attention of a fellow German, Schott, who was interested in glass-making, and who, in 1881, got into touch with him on the subject. As a result there were initiated by those workers the classical investigations at Jena, which gave the optical glass industry a new lease of life. Commencing in a small way with meltings of twenty to sixty grams, an attempt was made to study the optical effect of all the elements capable of entering into the composition of glass. The scale of the work quickly grew, and in twelve months meltings as large as ten kilograms were made. By the year 1884 a factory for the production of the new glasses was commenced, and was well supported both by the Prussian Diet and by the German opticians. Since its incorporation the Jena works has not only studied the chief problems of optical glass, but has successfully produced other types of glassware, such as chemical and thermal resistance glass. Of recent years, war-time necessity induced other English, American, and German firms to embark on the study and production of optical glass. In this connection the systematic work of C. J. Peddle on the effect of the chief glass-making oxides upon the density, optical constants, and stability of optical glasses has produced a wealth of information, and is perhaps the most important investigation in this direction which has, as yet, been published.

(15) **Production of Glass in the United Kingdom.***—The history of glass manufacture in the United Kingdom during the past hundred years may be divided into three periods. The first, up to 1845, was one of extreme difficulty, due to excessive taxation of the industry by an unsympathetic Government, and to the host of crippling regulations incidentally framed in order to prevent evasion of customs dues. By these laws, owners and managers were rendered almost powerless in their own establishments, and a horde of salaried officials was fastened upon an industry which threatened to die of strangulation.

That growth was slow, even amongst a rapidly increasing population with ever-growing requirements, is indicated by the following table of production:

TABLE I.—PRODUCTION OF GLASSWARE IN THE UNITED KINGDOM.

<i>Year.</i>	<i>Crown, Flint, Plate and White.</i>	<i>Plate.</i>	<i>Crown and Sheet.</i>	<i>Broad.</i>	<i>Common Bottle.</i>
	<i>Cwts.</i>	<i>Cwts.</i>	<i>Cwts.</i>	<i>Cwts.</i>	<i>Cwts.</i>
1800	71,200	—	82,070	20,430	329,800
	<i>Flint and Phial</i>				
1820	52,880	10,000	98,870	8,030	289,930
1840	100,160	27,060	130,200	8,510	462,070

* W. E. S. Turner, *J. Soc. Glass Tech.*, 1922 **6**, 108.

From this date (1845), when by dint of great effort taxation had been removed and manufacturers were again unhampered, trade increased by leaps and bounds, and for a number of years the industry was extremely flourishing. The tide of prosperity turned about the year 1875, and after this date keen competition of foreign manufacturers, using newer and more efficient processes, slowly caused a decline. We may best illustrate this falling off by tables showing exports and imports during the past sixty years:

TABLE II.—BRITISH EXPORTS AND IMPORTS OF GLASSWARE.

Year.			Exports.	Imports.	Ratio (<i>Exports.</i> <i>Imports.</i>)
			£	£	
1860	653,198	244,218	2.67
1880	921,508	1,776,472	0.52
1900	1,033,605	3,199,511	0.32
1920	3,210,800	8,506,708	0.38

TABLE III.—BRITISH EXPORTS AND IMPORTS OF GLASSWARE FOR 1922.

Type of Glassware.		Exports.		Imports.	
		£	Cwts.	£	Cwts.
Tubing and rod	..	8,320	913	17,320	4,607
Scientific	..	60,671	—	64,793	—
Illuminating	..	49,613	5,101	405,475	150,266
Machinery	..	43,461	5,058	1,356	133
Optical	..	29,063	1,087	1,260	119
Domestic and fancy	..	170,696	14,192	1,436,122	441,065
Plate and sheet	..	1,229,792	546,246	1,547,210	870,415
Bottles and jars	..	457,203	—	963,801	—
Unenumerated	..	39,509	5,820	37,051	10,723
Total	..	£2,088,328	578,426	£4,474,298	1,477,418

The years of war, 1914-1919, witnessed a great revival in the United Kingdom, freedom from competition and urgency of requirements serving as a fillip to the industry. Now that unlimited competition has again been introduced, bad times have returned, and it remains to be seen whether the country can successfully hold her own in the world's markets.

Experience has taught bitter lessons, and it may be prophesied that not again, through lack of adequate materials and machinery, will the industry fail to hold its own in these islands; for manufacturers have resolved to meet the competition of foreign countries, as far as possible, by exploiting to the full all the scientific aid which is available for them.

(16) **Production of Glass in Other Countries.**—Turning now to the world in general, we can best compare the relative rates of growth in

different countries by tables showing the increase in the number of works and of workers in the closing period of last century:

TABLE IV.—GLASS FACTORIES AND GLASS WORKERS IN THE MOST IMPORTANT GLASS-PRODUCING COUNTRIES.

	1874.		1895.	
	<i>Factories.</i>	<i>Workers.</i>	<i>Factories.</i>	<i>Workers.</i>
Germany	348	?	312	71,300
Austria	203	60,000	200	50,000
United Kingdom ..	240	21,170	230	22,000
France	175	22,830	200	50,000
United States ..	213	17,243	294	50,000
Russia	165	?	200	20,000
Belgium	68	12,000	70	22,000
Italy	46	2,000	50	10,000
Holland	23	1,100	35	3,000

Most remarkable of all has been the enormous growth of glass-making of all kinds in the United States of America during the past century. It is well indicated in our closing table:

TABLE V.—COMPARATIVE SUMMARY OF GLASS MANUFACTURES IN UNITED STATES OF AMERICA.

	1860.	1880.	1900.	1919
Number of establishments ..	112	169	355	371
Capital (in dollars)	6,133,666	18,804,599	61,423,903	215,680,436
Total officials and workpeople	9,016	24,177	55,086	83,656
Value of products (in dollars) ..	8,775,155	21,154,571	56,539,712	261,884,080
Number of pot furnaces ..	—	285	451	330
Number of tank furnaces ..	—	—	206	609

CHAPTER II

THE BASIS OF GLASS TECHNOLOGY

(17) **The Sciences Concerned.**—It is necessary for one who wishes to grasp successfully the principles underlying the process for the production of glass on a commercial scale to possess some knowledge of the sciences upon which glass technology is founded. The three most important are chemistry, physics, and engineering. It is not proposed, in this book, to go deeply into the purely theoretical side of these sciences, but they will be often referred to and applied, so that wherever the reader finds difficulty in grasping the points at issue, he is recommended to consult textbooks upon the subjects in question.

The chemical knowledge upon which the making of good glass depends is fundamental, but, until recent years, has been sadly neglected. It has been the custom to construct batches from *formulae* handed down from generation to generation, and often jealously guarded, but no knowledge of the changes involved during the process of manufacture was deemed necessary. As a result, when slight deviations from the normal conditions occurred, usually no one was available who could set matters right, and difficulty and even disaster followed. We may cite, for instance, the variation of composition of the batch materials. It is now known that a small change in the proportion of certain substances present in the glass (*i.e.*, iron oxide, alumina, etc.) makes great differences in the appearance or properties of the product obtained. Again, variations of moisture content in batch materials may affect substantially the amounts of the various oxides entering the glass, and their ratio to one another.

To one versed in chemistry the variations indicated are at once seen to be vital; they can be determined by anyone possessing a knowledge of chemical analysis, and, when this is done, the batch can be altered accordingly, so that the glass may remain constant in composition. The older glass manufacturers were also entirely at the mercy of those who provided them with materials, and even in cases where substances of good average purity were regularly supplied, it was not impossible, and even probable, that now and again compounds unfit for use, from the point of view of purity, were delivered. In general, no means but those of chemical analysis would serve to detect and reject the faulty materials.

Turning to the subject of the production of heat necessary for melting, knowledge of the heat value of the fuel, and of the composition of the gases evolved, are needful to enable one to provide a burning mixture of the requisite heating capacity. It is possible, though not always satisfactory, to obtain a regular check on the composition of material

from outside analytical sources, but it may prove expensive, and could often be rendered unnecessary by the application of a few simple tests.

Where, in spite of precautions, difficulties actually occur (and we may name in this category *devitrification* and the production of *stony metal*) through inefficient batch-mixing, too low a temperature of founding, or attack on the refractories, one who is equipped with some chemical knowledge will be more likely to get to the root of the trouble than one who is totally unversed.

(18) **The Chemical Basis.**—The basic chemical principle upon which all the other phenomena depend is that all individual substances can be divided into two classes—namely, *elements* and *compounds*. There are about eighty elements in nature, each with its own distinct properties, and, by chemical means alone, incapable of being destroyed or turned into any other element. Ultimately each element consists of minute particles of ultra-microscopic size, of which there are many millions in a cubic millimetre, and which receive the name of *atoms*. Atoms are the fundamental units, or bricks, used by nature in building chemical substances. For convenience of expression, “*symbols*” are used, consisting of one or two letters, by which single atoms of any element may be represented. “H” stands for one atom of *hydrogen*, “Si” for an atom of *silicon*. A table of the symbols of glass-making elements is appended (see Table VI.). The weights of single atoms of each element are

TABLE VI.—SYMBOLS, ATOMIC WEIGHTS, AND USUAL VALENCIES OF THE ELEMENTS.

Name of Element.	Symbol.	Atomic Weight.	Usual Valency.	Name of Element.	Symbol.	Atomic Weight.	Usual Valency.
Aluminium ..	Al	27.1	3	Magnesium	Mg	24.3	2
Antimony ..	Sb	120.2	3 or 5	Manganese	Mn	54.9	—
Argon ..	A	39.9	—	Nickel	Ni	58.7	2
Arsenic ..	As	75.0	3 or 5	Nitrogen ..	N	14.0	3 or 5
Barium ..	Ba	137.4	2	Oxygen ..	O	16.0	2
Bismuth ..	Bi	208.0	3 or 5	Phosphorus	P	31.0	5
Boron ..	B	11.0	3	Platinum ..	Pt	195.2	2 or 4
Cadmium ..	Cd	112.4	2	Potassium ..	K	39.1	1
Calcium ..	Ca	40.1	2	Rhodium ..	Rh	102.9	—
Carbon ..	C	12.0	4	Selenium ..	Se	79.2	4 or 6
Chlorine ..	Cl	35.5	1	Silicon ..	Si	28.3	4
Chromium ..	Cr	52.0	—	Silver ..	Ag	107.9	1
Cobalt ..	Co	59.0	2	Sodium ..	Na	23.0	1
Copper ..	Cu	63.6	2 or 1	Sulphur ..	S	32.1	4 or 6
Fluorine ..	F	19.0	1	Tellurium ..	Te	127.5	4 or 6
Gold ..	Au	197.2	3	Tin ..	Sn	118.7	2 or 4
Hydrogen ..	H	1.0	1	Titanium ..	Ti	48.1	4
Iridium ..	Ir	193.1	3 or 4	Tungsten ..	W	184.0	4 or 6
Iron ..	Fe	55.8	2 or 3	Uranium ..	U	238.2	—
Lead ..	Pb	207.2	2	Zinc ..	Zn	65.4	2
Lithium ..	Li	6.9	1	Zirconium ..	Zr	90.6	4

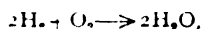
constant, or practically so. Since, individually, atoms are extremely small, it is usual to give only the relative weights of the atoms of different elements, taking the weight of an *oxygen* atom as 16.00. On this basis

the weight of an atom of hydrogen is 1.008 and of one of silicon is 28.3. The numbers so obtained are known as the *atomic weights* of the elements, and are given, with the symbols, in the above table. Atoms of the same or of varying elements can be caused to join together in groups of definite numbers, called *molecules*, and when the atoms of more than one element are concerned, compounds result. The forces holding atoms together as molecules are probably electrical.

According to present knowledge, any one atom may *directly* hold, or combine with, from one to eight other atoms but not more. A hydrogen atom can combine directly with one other atom only, whatever the element may be to which it is joined; on the other hand, an oxygen atom may combine with two hydrogen atoms, and a carbon atom with four. The combining power of an atom is called the *valency*, and hydrogen is stated to be *mono-valent*, oxygen *di-valent*, and carbon *tetra-valent*.

In nature, free atoms of hydrogen do not occur, but the atoms are bound together in pairs, forming molecules of hydrogen. The hydrogen molecule may be expressed as H—H (where the valency is expressed by a hyphen), or better, H₂. Molecules of oxygen also contain two atoms of the element, being written O—O, or O₂.

A molecule of water consists of an atom of oxygen bound to two atoms of hydrogen—i.e., H—O—H, or H₂O. When hydrogen is burned in oxygen, water results, and the reaction may be expressed in the form of a chemical equation:—



which, being interpreted, means that two molecules of hydrogen, each containing two atoms of the element, react with one molecule of oxygen, also containing two atoms, to give two molecules of water, each containing two atoms of hydrogen and one of oxygen. It will be seen that the total number of atoms on one side of the equation is equal to that on the other—that is, no atoms have been either created or destroyed in the course of the reaction. All compounds can be expressed as groups of symbols known as *formulae*. The formula for water is H₂O, whilst silicon (tetra-valent) combines with oxygen to give a molecule consisting of one atom of silicon and two of oxygen, a compound known as *silicon dioxide* or *silica*, and having the formula $\text{Si} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}$ or SiO₂.

We may here, with advantage, distinguish between a *physical* and a *chemical* change. The former consists of any change in the nature or properties of a substance which does not involve a variation of chemical composition. As examples we may cite the change of water into steam or ice (both of which also have the molecular formula H₂O), or of the solution of sugar in water. If, on the other hand, reactions occur, resulting in the regrouping of the atoms and the formation of molecules of new compounds, the same are known as chemical changes.

In defining the combining power of valency of the atoms, we have so far only considered the elements to have fixed valencies, a condition far from exact, since many possess two or more differing values of valency. Iron (symbol Fe) is a typical example. It may be either di-valent,

(Fe $\cdot\cdot$), when it forms *ferrous* compounds, or tri-valent, (Fe \equiv), when it forms *ferric* compounds. The formula for *ferrous oxide* is Fe=O, and of *ferrous chloride* Fe $\begin{smallmatrix} \diagup \text{Cl} \\ \diagdown \text{Cl} \end{smallmatrix}$ or FeCl₂, (since *chlorine* is mono-valent in this case). *Ferric oxide* has the formula Fe $\begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}$ or Fe₂O₃, and *ferric chloride* Fe $\begin{smallmatrix} \diagup \text{Cl} \\ \diagdown \text{Cl} \end{smallmatrix}$ or FeCl₃. Manganese (Mn) has a much greater variation of valency. It may be di-valent (MnO), tri-valent (Mn₂O₃), tetra-valent (MnO₂), hexa-valent (MnO₃), and hepta-valent (Mn₂O₇).

(19) **Acids**.—Compounds of oxygen with other elements are called *oxides*; they are widely spread in nature, and, since they are extremely important from the point of view of glass-making, we will consider them in more detail. Where oxides of elements that are *non-metallic* in character (carbon, sulphur, nitrogen, phosphorus) occur, the oxides are generally acidic in character. Acids can be defined, in that they usually have a sour taste, are corrosive, redden the blue vegetable colouring matter litmus, and contain hydrogen, part or all of which can be replaced when the acid is treated with a metal, metallic oxide, or metallic hydroxide. By dissolving the above named acid oxides in water we obtain acids—namely:—

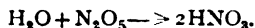
(1) *Carbonic acid*, H₂CO₃, obtained by dissolving *carbon dioxide*, CO₂, in water:—



(2) *Sulphurous acid*, H₂SO₃, from *sulphur dioxide*, SO₂, and water.

(3) *Sulphuric acid*, H₂SO₄, from *sulphur trioxide*, SO₃, and water.

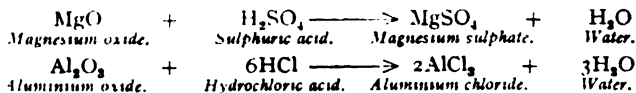
(4) *Nitric acid*, HNO₃, from *nitrogen pentoxide*, N₂O₅, and water—i.e.,



(5) *Phosphoric acid*, H₃PO₄, from *phosphorus pentoxide*, P₂O₅, and water.

(6) *Silicic acid*, H₂SiO₃, and *boric acid*, H₂B₄O₇, are compounds of a similar nature. It is necessary to add that there are some important acids not containing oxygen, such, for example, as *hydrochloric acid* (HCl).

(20) **Bases**.—Most *metallic* oxides are not acidic, but, on the contrary, will react with acids to give water and compounds known as *salts*, in which the hydrogen of the acid is replaced by the metal. Below are two typical reactions between metallic oxides and acids:—



To such oxides we give the name of "*bases*." Bases, then, are substances which will replace the acidic hydrogen of acids by a metal, or, as we say, will neutralise the acids. Some basic oxides dissolve in water and then can affect litmus, turning red litmus blue. Oxides having this property are called "*alkaline*" oxides or "*alkalis*." Examples of alkalis are the oxides of sodium (Na₂O), potassium (K₂O), and calcium (CaO), as also is a solution of ammonia (NH₄OH). Examples of basic

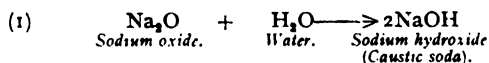
oxides not soluble and not alkaline are lead oxides, iron oxides, and copper oxide; the bulk of basic oxides are of this type.

(21) **Salts.**—It has been stated that salts are substances obtained when acids have been neutralised by bases. They have, in general, no action on litmus, but this is not universally the case, since *sodium carbonate* and *sodium phosphate* are alkaline, turning red litmus blue. Again, *potassium bi-sulphate* is a salt in which only half the hydrogen has been replaced—*i.e.*, KHSO_4 —and it is acid in character, turning blue litmus red. *Salt-cake* (Na_2SO_4), *limestone* (CaCO_3), and *nitre* (KNO_3) are all examples of the class of substances termed salts.

The manufacture of glass consists largely in making certain salts.

(22) **The Preparation of Salts.**—Several methods of producing salts are available, but we need only outline four.

(1) BY NEUTRALISING AN ALKALI WITH AN ACID.—*Sodium nitrate* is the salt obtained by neutralising a solution of nitric acid with a solution of *caustic soda* (NaOH). Caustic soda is the alkali obtained when *sodium oxide* is dissolved in water. The equation representing the reaction between sodium oxide and water is:—



and that between caustic soda and nitric acid:—



The equation (2) can be represented quantitatively in the following manner:—Since the atomic weight of *sodium* is 23, that of oxygen 16, and that of hydrogen 1, the *molecular weight* of caustic soda is

$$23 + 16 + 1 = 40.$$

The molecular weight of nitric acid is

$$\left. \begin{array}{l} \text{H} = 1 \\ \text{N} = 14 \\ 3 \times \text{O} = 3 \times 16 = 48 \end{array} \right\} \text{Total } 63.$$

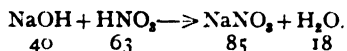
The molecular weight of sodium nitrate is

$$\left. \begin{array}{l} \text{Na} = 23 \\ \text{N} = 14 \\ 3 \times \text{O} = 48 \end{array} \right\} \text{Total } 85;$$

and of water

$$\left. \begin{array}{l} 2 \times \text{H} = 2 \\ \text{O} = 16 \end{array} \right\} \text{Total } 18.$$

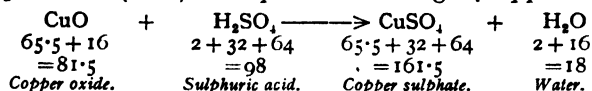
We may now re-write the equation (2) thus:—



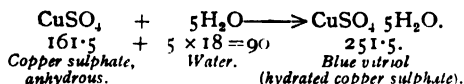
This means that if we have a knowledge of the equation representing the reaction between two chemical substances, we can, from a table of atomic weights, calculate the relative amounts of the substances required for complete reaction, and the relative weights of the substances obtained. The above equation tells us that, if we mix 40 parts by weight of caustic soda with 63 parts of nitric acid (whether the parts be grams, pounds, or tons, so long as the same unit is consistently em-

ployed), we shall obtain 85 parts by weight of sodium nitrate and 18 parts of water. If we have excess of one of the reagents, that excess will be left unchanged at the close of the reaction; in the above case, if we employed 40 lbs. of caustic soda and 70 lbs. of nitric acid, we should still obtain 85 lbs. of sodium nitrate and 18 lbs. of water, but we should also have $70 - 63 = 7$ lbs. of free nitric acid left unattacked.

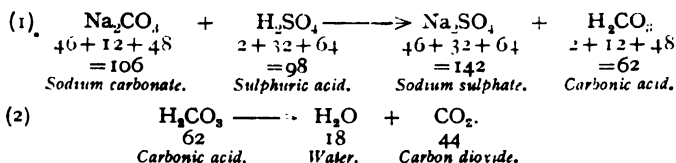
(2) BY DISSOLVING A BASE IN AN ACID.—This method is similar to the preceding one, the only difference being that the base is not soluble in water and must be added directly to the acid. An example is the solution of black *copper oxide* (CuO) in *sulphuric acid* to give *copper sulphate* :—



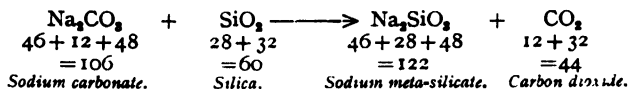
Here 81.5 parts by weight of copper oxide and 98 parts of the acid produce 161.5 parts of copper sulphate and 18 parts of water. If the solution is now concentrated, the copper sulphate crystallises out, but the crystals also contain *water of crystallisation*, giving the well-known "blue vitriol" :—



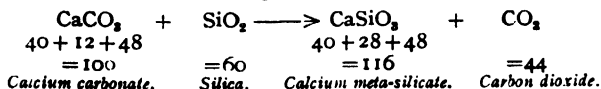
(3) BY THE ACTION OF AN ACID ON A SALT.—Instead of using a base, salts may be employed to react with acids. Sulphuric acid acts on the sodium salt of carbonic acid (sodium carbonate, Na_2CO_3) to give *sodium sulphate* and carbonic acid. The carbonic acid is unstable and breaks up into carbon dioxide and water :—



The method is sometimes varied, particularly in the practice of glass-making, by using an acidic oxide instead of an acid. Sodium carbonate is acted on by the acidic oxide silica at high temperatures to give *sodium meta-silicate* and carbon dioxide :—

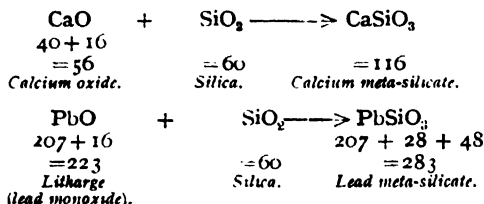


The latter form of the reaction resolves itself into a replacement of one acid oxide in a salt (*i.e.*, CO_2) by a second acidic oxide (SiO_2). Another important glass-forming reaction of a similar nature is that between calcium carbonate and silica to give *calcium meta-silicate* :—



* Anhydrous copper sulphate is white.

(4) **BY THE DIRECT UNION BETWEEN AN ACIDIC OXIDE AND A BASIC OXIDE.**—Typical reactions of this type are those between *calcium oxide* and silica and *lead oxide* and silica:—



(23) Salts Used in Glass-Making or Occurring in Glass-Making Practice.

(i) Salts of sulphuric acid, (H_2SO_4), containing the group $-\text{SO}_4$, and called *sulphates*: sodium sulphate (salt-cake), Na_2SO_4 .

(ii) Salts of sulphurous acid, (H_2SO_3), containing the group $-\text{SO}_3$, and called *sulphites*: sodium sulphite, (Na_2SO_3), obtained by the reduction of salt-cake (p. 98).

(iii) Salts from the weak acid hydrogen sulphide (sulphuretted hydrogen, H_2S) containing the sulphur atom $-\text{S}$ and called *sulphides*: cadmium sulphide, CdS , a yellow colouring agent; sodium sulphide, Na_2S , sometimes used in making copper ruby glass.

(iv) Salts of carbonic acid, (H_2CO_3), containing the group $-\text{CO}_3$, and called *carbonates*: sodium carbonate, (Na_2CO_3), potassium carbonate, (K_2CO_3), calcium carbonate, (CaCO_3), barium carbonate, (BaCO_3), magnesium carbonate, (MgCO_3).

(v) Salts of nitric acid, (HNO_3), containing the group $-\text{NO}_3$ and called *nitrates*: sodium nitrate, (NaNO_3), potassium nitrate, (KNO_3).

(vi) Salts of hydrochloric acid, (HCl), containing the atom $-\text{Cl}$ and called *chlorides*: sodium chloride, (NaCl), potassium chloride, (KCl).

(vii) Salts of hydrofluoric acid, (HF), containing the atom $-\text{F}$ and called *fluorides*: sodium fluoride, (NaF), calcium fluoride, (CaF_2), cryolite, (sodium aluminium fluoride, Na_3AlF_6).

(viii) Salts of the silicic acids. There are several silicic acids, the chief being (a) meta-silicic acid, (H_2SiO_3), which gives *meta-silicates* containing the group $-\text{SiO}_2$: sodium meta-silicate, (Na_2SiO_3), calcium meta-silicate, (CaSiO_3), lead meta-silicate, (PbSiO_3).

(b) Ortho-silicic acid, (H_4SiO_4), giving *ortho-silicates* containing the group $-\text{SiO}_4$: magnesium ortho-silicate, (*olivine* $-\text{MgSiO}_4$).

(c) Di-silicic acid, ($\text{H}_2\text{Si}_2\text{O}_5$ or $\text{H}_6\text{Si}_2\text{O}_7$), giving *di-silicates* with the groups $-\text{Si}_2\text{O}_5$ or $-\text{Si}_2\text{O}_7$: barium di-silicate, (BaSi_2O_5), magnesium di-silicate, (*serpentine* $\text{Mg}_3\text{Si}_2\text{O}_7$).

(d) Hypothetical tri-silicic acids, ($\text{H}_4\text{Si}_3\text{O}_8$, $\text{H}_{10}\text{Si}_3\text{O}_{11}$, $\text{H}_{14}\text{Si}_3\text{O}_{13}$), with the groups $-\text{Si}_3\text{O}_8$, $-\text{Si}_3\text{O}_{11}$, or $-\text{Si}_3\text{O}_{13}$: *felspar* (*orthoclase*) or *potassium aluminium tri-silicate*, ($\text{Al}_2\text{K}_2(\text{Si}_3\text{O}_8)_2$ or $\text{Al}_2\text{O}_3 \cdot \text{K}_2\text{O} \cdot 6\text{SiO}_2$).

(ix) Salts of the boric acids. (a) Meta-boric acid, (HBO_2), giving *meta-borates*: sodium meta-borate NaBO_2 ; (b) ortho-boric acid, (H_3BO_3), giving *ortho-borates*: calcium ortho-borate, $\text{Ca}_3(\text{BO}_3)_2$; (c) bi-boric or pyro-boric acid, $\text{H}_2\text{B}_4\text{O}_7$, giving *bi- or pyro-borates*: sodium bi-borate (*borax*), $\text{Na}_2\text{B}_4\text{O}_7$.

composition of any glass in this form from a knowledge of the amounts of the materials used (approximately), or from an analysis of the glass.

Not all the meltings obtained from calcium oxide, sodium oxide and silica in varying proportions give glass. Indeed, a small proportion only produce a transparent non-crystalline material of sufficient stability towards weathering to find successful employment. Fig. 2, a diagram of the system Na_2O , CaO , SiO_2 , best illustrates the point in question. It represents the work of Gelstharp and Parkinson.* All points within the equilateral triangle represent fused mixtures of the three oxides. The corners represent 100 per cent. of the three oxides, respectively, and the lines joining them, the various binary mixtures of the two components. Point **A** represents the mixture $2\text{Na}_2\text{O}.\text{SiO}_2$; **B**, $\text{Na}_2\text{O}.\text{SiO}_2$; **C**, $\text{Na}_2\text{O}.2\text{SiO}_2$; and **E**, $\text{Na}_2\text{O}.5\text{SiO}_2$. The composition of a melt given by point **X** is obtained by drawing lines **X1**, **X2**, and **X3** parallel to the axes. The silica content of the mixture is represented by **X2**, the soda content by **X1**, and the lime content by **X3**. Whatever the position of **X** in the triangle, the sum of lines **X1**, **X2**, and **X3** is equal to the length of the side of the triangle and represents 100 per cent. of the constituents. When **X** is situated as in the diagram, the mixture would be SiO_2 16 per cent., CaO 66 per cent., Na_2O 18 per cent.

According to Gelstharp and Parkinson, below the line **AH** ($2\text{Na}_2\text{O}.\text{SiO}_2$ and $\text{CaO}.\text{SiO}_2$) basic slags only are obtained and infusible mixtures of silicates. Between **AH** and **BG**, transparent glass is obtained only on rapid cooling, otherwise an opaque crystalline mass results. Between **BG** and **EG** is transparent glass proper, including technical glass. Above **EG**, only opalescent or opaque glasses are got on slow cooling. Below **CF**, the glasses are mechanically weak, do not readily resist dilute acids, carbon dioxide, water, etc., and tend to devitrify or crystallise readily. Line **PD** is the boundary line for good glass, and the sodium oxide content is here 22 per cent. of the silica content. The shaded portion **DELM** represents commercial glasses. It is divided by line **ON**, denoting the ratio $2\text{Na}_2\text{O}$, CaO (part of line **JR**). Only in the portion **DEON** can soda-ash alone be used as a source of alkali. In the portion **OLMN** some salt-cake must be employed or white scum and flakes are produced. The diagram is named the *ternary diagram* of the system sodium oxide—calcium oxide—silica.

(25) **The Physical Basis.**—It will be evident that a knowledge of the physical properties of glasses, the rate of *thermal expansion*, and of *heat conductivity*, the *refractive index*, etc., and of the variation of these with the chemical composition of the glass, is of great importance. At the present time such knowledge is fragmentary and incomplete, but already sufficient information has been gained to improve materially some types of ware, notably heat-resisting and optical glasses. A further application is the guidance it affords in the choice of glass suitable for particular methods of working, as for hand-made or machine-made goods.

* *Trans. Amer. Cer. Soc.*, 1914, **16**, 109; these results are based on meltings made in platinum crucibles at a temperature probably not exceeding 1400°C .

CHAPTER III

THE PHYSICAL PROPERTIES OF GLASS

(26) **Chemical Constitution and Additive Properties.**—The exact chemical constitution of glass is so little understood that the actual effect of each chemical compound present upon the physical properties cannot be stated. Quite useful work has been done, however, upon the lines of determining the effect of the various oxides which form the basis of the different glasses. Many physical properties, by this means, have been shown to be “*additive*” in character, or at least approximately so. An additive property is one which is dependent not only upon the oxides which the glass contains, but also upon the relative amounts of these which are present. Where, for instance, a glass contains a number of oxides, **A, B, C . . .**, the percentage weights of which are $p_A, p_B, p_C . . .$ respectively, then the value of any additive physical constant will be given by the equation $K = p_A x_A + p_B x_B + p_C x_C . . .$, where $x_A, x_B, x_C . . .$ are constants for the particular oxides and represent the effect of one per cent. of the oxide upon the property in question. The first systematic study of the problem in the light of additive relationships was that of the Jena school of investigators, Schott and his collaborators, who first determined constants for *density*, *coefficient of thermal expansion*, etc. The values obtained, in spite of the fact that later determinations by other observers have called into question a number of the results, have proved remarkably helpful in suggesting the types of glass best fitted for certain purposes, and in enlarging the scope of uses to which glassware can be placed. Below will be found a consideration of a number of physical properties approached from the viewpoint of chemical constitution.

Mechanical Properties.

(27) **Density.**—A knowledge of the density of glass is important in several ways. The pressure exerted by fluid glass upon the walls of a containing vessel is proportional to the density of the glass; hence the power of resistance to bulging which pot walls must possess is dependent upon the density of the glass within the pot. Further, waves, cords, and striæ in glass often correspond to layers of varying density, and are a fruitful source of faulty ware, particularly that for optical purposes. Since also refractive index varies with density to a very large extent, a knowledge of density is useful in the case of optical glasses. Winkelmann and Schott calculated densities from the formula $\frac{100}{D} = \frac{p_1}{d_1} + \frac{p_2}{d_2} + \frac{p_3}{d_3} . . .$, where

D is the density of the glass, $p_1, p_2, p_3 \dots$ the percentages of the oxides present, and d_1, d_2, d_3 the densities of the oxides in the combined states. It was pointed out that the densities in the combined state were somewhat greater than those of the oxides in the free state, indicating a condensation during the formation of the glass. Winkelmann and Schott's* figures for the effect of the varying oxides were:—

TABLE VII.—WINKELMANN AND SCHOTT'S DENSITY FACTORS.

Oxide.	Density.		Oxide.	Density.		Oxide.	Density.	
	In Glass.	Free.		In Glass.	Free.		In Glass.	Free.
PbO	0.6	0.32	Al ₂ O ₃	4.1	3.85	Na ₂ O	2.6	2.55
ZnO	5.9	5.65	MgO	3.8	3.40	P ₂ O ₅	2.55	2.38
BaO	7.0	5.00	CaO	3.3	3.15	SiO ₂	2.3	2.17
As ₂ O ₅	4.1	4.09	K ₂ O	2.8	2.66	B ₂ O ₃	1.9	1.46

The property which is additive is here not the density, but its reciprocal, $\frac{1}{D}$, known as the *specific volume*—that is, the volume occupied by one gram of material. The values quoted only gave approximate results in the calculation of densities, and various modifications have been suggested.

Tillotson,† keeping the SiO₂ value at 2.3, modified the CaO to 4.1, the MgO to 4.0, the Na₂O to 2.8 and Al₂O₃ to 2.75.

Baillie‡ gave an alternative formula $\frac{P}{D} = \frac{p_1}{d_1} + \frac{p_2}{d_2} + \frac{p_3}{d_3} \dots$, where P was the total percentage of the oxides found by analysis, whilst his values for the effect of the oxides were:—

TABLE VIII.—BAILLIE'S DENSITY FACTORS.

Oxide.	Factor.	Oxide.	Factor.
SiO ₂	2.24	CaO	4.30
Al ₂ O ₃	2.75	MgO	3.25 (4.3 when alkalis absent)
B ₂ O ₃	3.00	PbO	10.30
As ₂ O ₅	2.90	K ₂ O	3.20
ZnO	5.94	Na ₂ O	3.20
BaO	7.20		

English and Turner§ have obtained rather more concordant results than other observers by using the following values:—SiO₂ 2.20, Na₂O 3.47, MgO 3.38, Al₂O₃ 2.75. Peddle|| holds that although specific volume is

* For this and other factors by Winkelmann and Schott see *Jena Glass Hovestadt*, translated by J. D. and A. Everett, London, 1902.

† *J. Ind. Eng. Chem.*, 1912, 4, 246.

‡ *J. Soc. Chem. Ind.*, 1921, 40, 141 T.

§ *J. Soc. Glass Tech.*, 1920, 4, 156.

|| *Ibid.*, 1920, 4, 8.

approximately additive, the change caused by the addition of one per cent. of any oxide is dependent upon the amount of that oxide already present, and where large amounts of any oxide occur, the results deviate largely from the values calculated from Winkelmann and Schott's figures.

As an example of the use of the above factors, we give in Table IX. the actual density of a glass the composition of which is stated, and the values calculated by using the constants of (1) Winkelmann and Schott, (2) Tillotson, (3) Baillie, and (4) English and Turner. The example serves to indicate the method of calculation.

TABLE IX.—THE CALCULATION OF DENSITY.

Composition of the Glass (per Cent.).	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃ *	CaO	Na ₂ O	Density (D).	
	72.10	6.84	0.085	0.12	20.62	Calculated.	Observed.
Density: Method (1) ..	$\frac{72.10}{2.3} + \frac{6.84}{4.1}$			$+ \frac{0.12}{3.3}$	$+ \frac{20.62}{2.6} - \frac{100}{D}$	2.439	2.4181
Method (2) ..	$\frac{72.10}{2.3} + \frac{6.84}{2.75}$			$+ \frac{0.12}{4.1}$	$+ \frac{20.62}{2.8} - \frac{100}{D}$	2.425	—
Method (3) ..	$\frac{72.10}{2.24} + \frac{6.84}{2.75}$			$+ \frac{0.12}{4.3}$	$+ \frac{20.62}{3.2} - \frac{99.76}{D}$	2.424	—
Method (4) ..	$\frac{72.10}{2.20} + \frac{6.84}{2.75}$			$+ \frac{0.12}{3.30}$	$+ \frac{20.62}{3.47} - \frac{100}{D}$	2.424	—

It must be understood that the condition of the glass is an important factor, and comparative results can only be obtained with completely annealed specimens.

(28) **Tensile Strength.**—Of great importance amongst mechanical properties is tensile strength, since the mechanical stability of glassware is greatly dependent upon it. The property is measured by the smallest weight which will cause the breakage of a rod of glass having a unit area of cross-section. According to Winkelmann and Schott, the coefficient for Jena glass varies between 3.5 and 8 kilograms per square millimetre (2 to 5½ tons per square inch), but difficulties in carrying out observations render the results somewhat variable.

Trautwine for other glasses gives rather lower figures (1 to 4 tons per square inch), whilst Kowalski's results are rather higher (5 to 6 tons per square inch).

According to Winkelmann the property is approximately additive and $P = p_1a_1 + p_2a_2 + \dots$, the factors a_1, a_2 , etc., being given as in Table X.

Correspondence between calculated and observed results was not very close, but the table indicates the relative position of the oxides. High silica content or the presence of appreciable amounts of calcium or zinc oxides makes for high tensile strength, whilst alkalis or magnesium oxide tend to give a low value of tensile strength.

* The iron oxide value is small and may be neglected.

TABLE X.—WINKELMANN'S FACTORS FOR TENSILE STRENGTH.

<i>Oxide.</i>	<i>Factor.</i>	<i>Oxide.</i>	<i>Factor.</i>	<i>Oxide.</i>	<i>Factor.</i>
SiO ₂	0.09	CaO	0.20	PbO	0.025
P ₂ O ₅	0.075	ZnO	0.15	Na ₂ O	0.02
B ₂ O ₃	0.065	BaO	0.05	K ₂ O	0.01
As ₂ O ₃	0.03	Al ₂ O ₃	0.05	MgO	0.01

In this case also, and, in general, for all physical properties, well annealed samples of glass are necessary to obtain comparative results.

(29) **Crushing Strength.**—The measure of crushing strength is the least force required just to break down a cube of glass of unit volume. The value is relatively much higher than that of tensile strength, and the property does not play such an important rôle in the mechanical stability of the glass as tensile strength. Winkelman and Schott, for Jena glass, gave values ranging from 60 to 126 kilograms per square millimetre, whilst approximate additive coefficients for the effect of one per cent. of oxide were given as follows:—

TABLE XI.—WINKELMANN AND SCHOTT'S FACTORS FOR CRUSHING STRENGTH.

<i>Oxide.</i>	<i>Factor.</i>	<i>Oxide.</i>	<i>Factor.</i>	<i>Oxide.</i>	<i>Factor.</i>
SiO ₂	1.23	MgO	1.1	Na ₂ O	0.52
As ₂ O ₃	1.00	Al ₂ O ₃	1.0	PbO	0.48
B ₂ O ₃	0.90	BaO	0.65	CaO	0.20
P ₂ O ₅	0.76	ZnO	0.6	K ₂ O	0.05

(30) **Elasticity.**—The displacement of the various particles of a body relatively to one another, which is produced when the body is acted upon by a system of forces, is called a *strain*. Substances which resist strains by setting up internal restoring forces are said to be elastic, and the restoring forces are named *stresses*. A measure of the elasticity of a body is given by the ratio of stress to strain—*i.e.*, Elasticity = $\frac{\text{stress}}{\text{strain}}$.

The greater the elasticity of a body the greater the stress or restoring force set up by the same strain. Low elasticity in glass will evidently favour mechanical endurance, tending to prevent dangerous stresses in badly distorted articles. Winkelman and Schott found Young's modulus of elasticity for a number of glasses by supporting rods of rectangular section upon knife edges, and weighting the centre of the rods. By noting the angle through which the ends of the rods bent from the horizontal, the amount of strain could be deduced. No completely generalised rule could be formulated, but they reached the conclusion that by dividing the glasses into groups, the approximate effect of one per cent. of the oxides in each group could be stated.

Clarke and Turner,* from an examination of a series of soda-lime

* *J. Soc. Glass Tech.*, 1919, 3, 260.

glasses, found the following factors (a in the general additive equation $p_1a_1 + p_2a_2 + \dots$) to give quite good results:— SiO_2 40, Na_2O 110, Al_2O_3 120, Fe_2O_3 120, CaO 240, MgO 300. An increase in the lime content was found to produce a marked increase in the elasticity of soda-lime glasses.

(31) **Hardness.**—Glass varies in hardness with variation of chemical composition. No very satisfactory method of measuring hardness has yet been devised however. Moh created a scale by taking as standards the following substances, placed in order of increasing hardness:—(1) Talc, (2) Rocksalt, (3) Calc-spar, (4) Fluorspar, (5) Apatite, (6) Felspar, (7) Quartz, (8) Topaz, (9) Sapphire, (10) Diamond. Comparative tests are made by noting which of the standards can be scratched by the article under observation. The method is not very satisfactory, and at the most gives a very rough qualitative result.

Auerbach attempted to find a quantitative value for the hardness of glass by noting the extent to which a sphere of sandstone could be pressed into a block of the glass without permanent deformation of the sphere or block. From his results he expressed the effect upon hardness of the individual oxides, his figures for each one per cent. of the oxides being:— Al_2O_3 , +10.1, ZnO , +7.1, K_2O , +3.9, SiO_2 , +3.32, BaO , +1.95, PbO , +1.45, P_2O_5 , +1.32, B_2O_3 , +0.75, Na_2O , -2.65, CaO , -6.3.

Lecrenier* states that the above figures are not at all suitable for specimens he has examined. He summarises the effect of the oxides thus:—(1) Soda glasses are, as a rule, harder than potash glasses containing an equal volume of silica. (2) For pure soda-lime glasses, hardness increases with increase of lime and decrease of soda. (3) Boric oxide gives great hardness to glass. (4) Lead glasses are increased in hardness by addition of soda and of lime.

Thermal Properties.

(32) **Specific Heat.**—The specific heat of a substance is given by the number of gram-calories of heat required to raise the temperature of one gram of the substance from 0°C. to 1°C. The specific heat of glass lies between 0.08 and 0.25. In this property also, additive relationships have been shown to exist, and the coefficients for the effect of one per cent. of the oxides are given in Table XII.

TABLE XII.—FACTORS FOR SPECIFIC HEAT.

Oxide.	Factor.	Oxide.	Factor.	Oxide.	Factor.
SiO_2	0.001913	Na_2O	0.002674	MgO	0.002439
B_2O_3	0.002272	K_2O	0.001860	PbO	0.000512
As_2O_3	0.001276	CaO	0.001903	ZnO	0.001245
P_2O_5	0.001903	BaO	0.000673		

It must be emphasised that the amount of heat required to raise the temperature of one gram of glass by 1°C. varies with the temperature of the glass.

(33) **Conductivity of Heat.**—The amount of heat passing between opposite faces of a cube of unit volume of material in unit time when the two faces are at a unit difference of temperature, is known as the coefficient of conductivity of heat of the material. The amount of heat Q which will pass through a slab of material in time T , the dimensions of which slab are—area of opposite surfaces, A , and thickness, e , and the temperatures of the opposite faces are t_1 and t_2 , will be $Q = k \frac{A(t_1 - t_2)T}{e}$

where k is the coefficient of thermal conductivity. The thermal conductivity of glass is relatively small and difficult to measure. Paalhorn and Focke* obtained values for the same glass which differed by as much as 30 per cent. Paalhorn has shown the property to be additive, and given the factors for one per cent. of the various oxides as in Table XIII.

TABLE XIII.—PAALHORN'S FACTORS FOR HEAT CONDUCTIVITY.

Oxide.	Factor.	Oxide.	Factor.	Oxide.	Factor.
K ₂ O	0·0010	B ₂ O ₃	0·0160	Al ₂ O ₃	0·0220
PbO	0·0080	P ₂ O ₅	0·0160	SiO ₂	0·0220
BaO	0·0110	Na ₂ O	0·0160	CaO	0·0320
ZnO	0·0160				

Glass with high thermal conductivity, such for instance as that containing much calcium oxide, will cool rapidly and must be quickly transferred to the lehr after manufacture, in order to prevent the temperature falling below the annealing point.

(34) **Thermal Expansion.**—The increase in length of unit length of any material when its temperature is raised by 1° C. is the coefficient of linear expansion, whilst the increase in volume of unit volume when the temperature is raised by the same amount, is the coefficient of cubical expansion. For solids, the cubical coefficient is approximately three times as great as the linear coefficient. The thermal expansion of glass varies with its composition and is of great importance. For instance, where glasses are "*flashed*" with layers of other glasses, the two layers must have very similar coefficients of expansion or one would tend to crack off from the other. Again, where metals have to be sealed into glass, as in wired window glass or electric lamp bulbs, the metal and glass must not greatly differ in coefficient of expansion, or the joining will be unsuccessful. Amongst the metals, platinum closely approaches ordinary glass in the rate of expansion and is the most successful for sealing into glassware, but recently alloys, particularly those of iron and nickel, have been produced with very similar coefficients to those of glass. The linear coefficient of soda-lime glasses varies between 0·000011 and 0·000008, that of lead crystal is about 0·000009. Laboratory glassware varies in expansion from 0·0000055 to 0·0000075.

* "*Jena Glass*," p. 212.

Pyrex glass* has even a lower value, possessing a linear coefficient of expansion of only 0.000032 ($19^{\circ}\text{C. to } 350^{\circ}\text{C.}$). In contrast to this, glasses can now be produced with a linear coefficient equal to that of iron (0.00013). The contrast between the most highly expanding and the least expanding glasses which can be made is very great, showing a ratio of the coefficients of 6 or 7 to 1. Winkelmann and Schott gave the factors shown in Table XIV. for cubical expansion:—

TABLE XIV.—WINKELMANN AND SCHOTT'S FACTORS FOR THERMAL EXPANSION.

<i>Oxide.</i>	<i>Factor.</i>	<i>Oxide.</i>	<i>Factor.</i>	<i>Oxide.</i>	<i>Factor.</i>
B_2O_3	0.1×10^{-7}	As_2O_3	2.0×10^{-7}	PbO	3.0×10^{-7}
MgO	0.1×10^{-7}	P_2O_5	2.0×10^{-7}	Al_2O_3	5.0×10^{-7}
SiO_2	0.8×10^{-7}	Li_2O	2.0×10^{-7}	CaO	5.0×10^{-7}
ZnO	1.8×10^{-7}	BaO	3.0×10^{-7}	K_2O	8.5×10^{-7}
				Na_2O	10.0×10^{-7}

English and Turner† have come to the conclusion that the following factors for cubical expansion more nearly represent the effect of the oxides named: SiO_2 , 0.15×10^{-7} , Na_2O , 12.96×10^{-7} , CaO , 4.89×10^{-7} , MgO , 1.35×10^{-7} , Al_2O_3 , 0.43×10^{-7} . Recalculation for a number of glasses using the revised factors gave results more nearly agreeing with the observed values. The rate of expansion is only linear below the annealing temperature range, over which Peters and Cragoe,‡ and also Pietenpol,§ have shown that much larger values are obtained.

As an example of the practical use of expansion coefficients we may take the following:—Glass A (below) is an opal base, and it is desired to find if the transparent blue glass B would be suitable for “flashing” the opal. Compositions of the two glasses are given, and from these we can calculate the coefficient of cubical expansion of each glass (using Winkelmann and Schott's factors).

GLASS A.

Percentage Composition.

SiO_2	64.58
PbO	0.94
CaO	9.98
Na_2O	1.12
K_2O	15.15
P_2O_5	7.64
As_2O_3	0.53
MnO	0.06

Thermal Expansion.

$64.58 \times 0.8 \times 10^{-7} =$	51.66×10^{-7}
$0.94 \times 3.0 \times 10^{-7} =$	2.82×10^{-7}
$9.98 \times 5.0 \times 10^{-7} =$	49.90×10^{-7}
$1.12 \times 10.0 \times 10^{-7} =$	11.20×10^{-7}
$15.15 \times 8.5 \times 10^{-7} =$	128.78×10^{-7}
$7.64 \times 2.0 \times 10^{-7} =$	15.28×10^{-7}
$0.53 \times 2.0 \times 10^{-7} =$	1.06×10^{-7}

Total .. 260.70×10^{-7}

* *Chem. Weekblad.*, 1920, 17, 465.

‡ *J. Opt. Soc. Amer.*, 1920, 4, 105.

† *J. Soc. Glass Tech.*, 1920, 4, 118.

§ *Chem. and Met. Eng.*, 1920, 23, 878

GLASS B.

Percentage Composition.

Thermal Expansion.

SiO ₂	72.47	72.47 × 0.8 × 10 ⁻⁷ =	57.98 × 10 ⁻⁷
PbO	1.08	1.08 × 3.0 × 10 ⁻⁷ =	3.24 × 10 ⁻⁷
CaO	8.03	8.03 × 5.0 × 10 ⁻⁷ =	40.15 × 10 ⁻⁷
Na ₂ O	2.18	2.18 × 10.0 × 10 ⁻⁷ =	21.80 × 10 ⁻⁷
K ₂ O	16.02	16.02 × 8.5 × 10 ⁻⁷ =	136.17 × 10 ⁻⁷
As ₂ O ₃	0.21	0.21 × 2.0 × 10 ⁻⁷ =	0.42 × 10 ⁻⁷
MnO	0.06	—	—
CoO	0.04	—	—
		Total ..	259.76 × 10 ⁻⁷

The glasses are quite suitable for the purpose specified.

(35) **Thermal Endurance.**—When glassware is subjected to sudden changes of temperature there is a tendency towards fracture, owing to the sudden stresses set up in the glass, and it is found that some types of glass are much more susceptible to breakage than others when such temperature changes occur. The power possessed by the glass to withstand, without breaking, sudden temperature changes, is known as its *thermal endurance*, and it depends upon several physical properties of the glass. Of these the most important are:—

(1) **Thermal Conductivity.**—Relatively high thermal conductivity favours thermal endurance, since the heat suddenly applied locally is then rapidly transferred through the material, and stresses due to unequal expansion are minimised.

(2) **Thermal Expansion.**—Sudden cooling of a piece of glass causes the surface layers rapidly to contract and throws them into a state of tension, whilst the interior is at the same time, but to a less degree, thrown into a state of compression. Conversely, when the glass is suddenly heated, the initial expansion of the outer layers sets up compressive stresses, with a smaller interior tension. The greater the rate of thermal expansion, the more intensely will the glass be stressed.

(3) **Tensile and Compressive Strengths.**—When the stresses in the glass exceed the tensile or compressive strengths fracture will occur. Where sudden cooling takes place, the greater stress is the tension in the surface layers, hence the important factor is tensile strength. Sudden heating causes large surface compression, and the safety of the glass is dependent upon compressive strength. Since crushing strength is always much greater than tensile strength, it is evident that glass will more readily stand sudden heating than sudden cooling.

(4) **Elasticity.**—Low elasticity favours thermal endurance, since the stress set up by local strains will be less than in glass with a high coefficient of elasticity.

Winkelmann and Schott gave as a measure of thermal endurance the expression $F = \frac{P}{\alpha E} \sqrt{\frac{K}{sc}}$, where **P** is the tensile strength, **E** the modulus of elasticity (Young's), α the coefficient of linear expansion, **K** the heat conductivity, *s* the density, *c* the specific heat, and **F** is called the coefficient of thermal endurance.

(36) **The Coefficient of Thermal Endurance.**—Practical determinations of thermal endurance were first carried out by the above observers,

who heated cubes of glass in water or glycerine to varying temperatures, and suddenly plunged them into water to ascertain the limiting differences of temperature which they could withstand.

Sullivan* heated eight or ten pieces of rod in a vertical electric furnace to a definite temperature and then, by removing a slide, dropped the rods all at once into water. The temperature difference at which 50 per cent. of the rods fractured was taken as a standard of comparison. A convenient comparison of the thermal endurance of common bottles, as practised at the Department of Glass Technology, Sheffield University, is arranged upon the above lines—that is, by heating a number of the bottles in water to temperatures of 65° C., 70° C., 75° C., etc., successively, and, after allowing them to stand at these temperatures until thermal equilibrium is reached, plunging them into water at 20° C. Where thermal endurance is good, 75 per cent. should withstand changes of 50° C. or over.

The thermal endurance of miners' lamp glasses has been studied and comparative tests suggested by Chesneau.† The first test consisted in heating the glasses in water to 100° C. and plunging them into water at 15° C., when not more than 50 per cent. should break. A second test, designed for glasses in lamps used where fire-damp occurs, consisted in standing the glass over, and in the axis of, a Berzelius burner with a ring-shaped flame, the flame to be inside the lamp glass and at 6 to 7 millimetres from the surface of the glass. With given conditions of the flame, not more than 20 per cent. of the glasses should fracture when heated for five minutes.

High thermal endurance is necessary in glasses for quite a number of purposes. For instance, in bottles designed to hold liquids which

TABLE XV.—COMPOSITION OF GLASSES WITH HIGH THERMAL ENDURANCE.

	THERMOMETER GLASSES.		CHEMICAL GLASSWARE.			LAMP GLASSES.		COOKING WARE.
	Jena 59	Jena 16	Old Jena.	A.‡	Macbeth Evans.	Jena Best.	Austrian "Sun" Brand.	"Pyrex."
SiO ₂ ..	72.86	66.58	64.60	65.5	73.0	73.88	76.78	80.5
Al ₂ O ₃ ..	6.24	3.84	6.24	2.5	1.0	2.24	0.72	2.0
CaO ..	0.35	7.18	Trace	—	0.7	Trace	6.52	0.3
ZnO ..	—	6.24	10.43	8.0	5.6	Trace	—	—
MnO ..	Trace	0.28	Trace	—	—	Trace	Trace	—
Fe ₂ O ₃ ..	Trace	Trace	Trace	—	0.4	Trace	Trace	0.3
Na ₂ O ..	9.82	14.80	9.71	10.0	10.8	6.67	11.14	4.4
K ₂ O ..	0.10	Trace	Trace	—	0.3	Trace	4.74	0.2
B ₂ O ₃ ..	10.43	0.91	8.70	9.0	3.6	16.48	—	11.8
MgO ..	0.20	0.17	0.32	5.0	4.3	Trace	0.24	0.1
As ₂ O ₃ ..	—	—	—	—	—	0.73	—	0.6
Sb ₂ O ₃ ..	—	—	—	—	0.6	—	—	—

* *J. Soc. Chem. Ind.*, 1916, **35**, 513.

† *Annales des mines*, 10th Series, 1908, **13**, 229; 1909, **15**, 33.

‡ Based upon Institute of Chemistry Formula, No. 8.

are heated (as when pasteurisation is carried out), in cooking ware, lamp glasses, chemical ware, thermometer tubing, etc. For the first class soda-lime glass is satisfactory, providing the alkali content is fairly low, and particularly when some alumina is introduced into the glass.

Where much greater differences of temperature are met with, radical changes in the composition of the glass are necessary. Very large amounts of silica are sometimes used, and the alkalis are cut down to as low a value as possible, whilst other oxides, such as boric oxide, zinc oxide or alumina, are generally introduced in appreciable amounts. We here append, in Table XV., the chemical composition of a number of glasses possessing high thermal endurance.

Electrical Properties.

(37) **The Specific Inductive Capacity** (*Dielectric constant*) varies with the composition of the glass, but the exact relationship between the two is not known, although high silica or soda tends to produce low values. The limits between which the constant lies are 5.4 and 8.5 at ordinary temperatures, but values increase with rising temperature.

The Dielectric Strength approximates to 10 kilo-volts per millimetre for window glass, though few observations are available.

Specific Electrical Resistance is higher in the case of more durable glasses, inferior types being better conductors, owing to the formation of a conducting surface film, due to weathering. Glass, when well annealed, has a higher resistance than when under strain. Gray and Dobbie* found that electrical conductivity was doubled for each 9° C. rise in temperature. It has been noted that glasses of compositions approaching those of true compounds have a high resistance. The following glass is stated to be a very good insulator, SiO₂ 33 per cent., Al₂O₃ 6 per cent., BaO 48 per cent., B₂O₃ 12 per cent.

APPENDIX.

Since the above chapter was written important results to which reference should be made are as follows:

1. The additive character of coefficient of thermal expansion, density and refractive index is not true of boric oxide containing glasses, maximum or minimum values occurring at certain compositions.†

2. J. Mori, after determining the coefficients of linear expansion of a number of sodium oxide, lead oxide, silica glasses, used the factors 0.05, 1.53, 1.53, and 0.45 respectively for SiO₂, CaO, Al₂O₃, and MgO, and calculated the corresponding factors for PbO and Na₂O to be 0.938 and 4.70 respectively.‡

3. V. H. Stott has proposed the formula $\theta_c - \theta_0 = \frac{P(1 - \sigma)}{Ea}$ for determining thermal endurance, where $\theta_c - \theta_0$ is the least temperature difference which can cause fracture, P is the tenacity, σ is Poisson's ratio, E is Young's modulus of elasticity, and a is the coefficient of expansion.§

* *Proc. Roy. Soc.*, 1898, **63**, 38; 1900, **67**, 197.

† W. L. S. TURNER, *J. Roy. Soc. Arts*, 1923, **71**, 401; ENGLISH AND TURNER, *J. Soc. Glass Tech.*, 1923, **7**, 73; TURNER, *J. Amer. Cer. Soc.*, 1924, **7**, 313.

‡ *J. Jap. Cer. Assoc.*, 1923, **368**, 176.

§ *J. Soc. Glass Tech.*, 1924, **8**, 139.

CHAPTER IV

THE OPTICAL PROPERTIES OF GLASS

Refractive Index.

(38) **Definition.**—When a ray of light passes from air into glass the ratio between the *sine* of the angle of incidence and the *sine* of the angle of refraction is a constant for the glass, and is called the *refractive index*. If **XY** (Fig. 3) is the glass surface, **AB** the *incident* ray, **BC** the *refracted* ray, and **DBE** the *normal* (or perpendicular) to the surface, **ABD** is the angle of incidence, **CBE** the angle of refraction, and $\frac{\text{sine ABD}}{\text{sine CBE}}$ is the refractive index, denoted generally by η . **Sine ABD** is given by the ratio $\frac{AD}{AB}$, where **AD** is the perpendicular on to the normal **BD**, whilst $\text{sine CBE} = \frac{CE}{CB}$. Where **AB** is taken equal in length to **BC**, the two being radii of the circle **XAYC**,

$$\frac{\text{Sine ABD}}{\text{Sine CBE}} = \frac{AD}{AB} \div \frac{CE}{BC} = \frac{AD}{CE}.$$

The index of refraction represents the ratio of the velocity of propagation of light waves in the glass to the velocity in air. The index of refraction

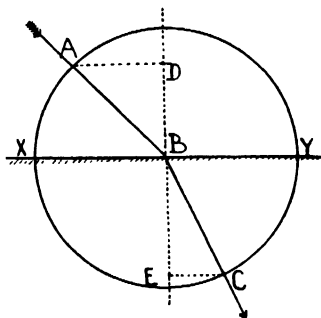


FIG. 3.—THE REFRACTION OF LIGHT.

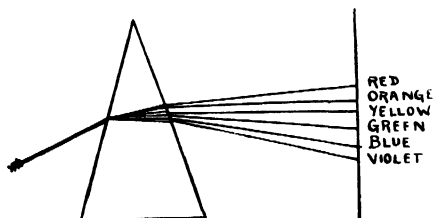


FIG. 4.—DISPERSION AND THE PRODUCTION OF THE SPECTRUM.

depends upon the composition of the glass and upon its physical state. It is also dependent upon the wave length of the light, being least for

light of longest wave length—i.e., red—and largest for the shortest waves—the violet.

For this reason, a ray of pure white light striking a glass surface is split up, and the rays spread out, the effect being known as *dispersion*. By passing the ray through a prism the dispersion is further increased at the second glass surface and the emergent light forms a continuous coloured band—the *Spectrum* (Fig. 4). In a comparison of the refractive indices of various glasses it is necessary to use light of the same wave length in each case, and the standards adopted are the characteristic *Fraunhofer* lines of the solar spectrum.

(39) **Spectra.**—The spectrum of sunlight is traversed by a great number of dark lines, the *Fraunhofer* lines, which are due to the absorption of certain colours from the light by the sun's or the earth's atmosphere. Examination of the spectra due to glowing gases or vapours proves them to be not continuous, but to consist of a series of bright lines in various parts of the spectrum. The *emission spectrum* of any particular element is characteristic, the position of the lines being fixed, and the spectrum can be used to determine the element itself. On the other hand, if a beam of white light be passed through a vapour or gas and, on its emergence, is examined by a prism, it is found to contain *absorption bands*, dark lines which correspond exactly in position with the lines which would be given by the heated vapour itself. This means that an element in the form of vapour or gas will abstract from white light traversing it the very same lines of colour which it will itself emit when heated. Thus, if a white light from a very hot body, such as an electric arc, is passed through a flame which is strongly coloured yellow by means of a sodium compound, two striking absorption bands are obtained in the orange yellow. When the white light is cut off, the light from the sodium flame will give two bright lines which occupy the same place, exactly, as did the dark absorption lines.

The *Fraunhofer* lines of the solar spectrum are absorption bands caused by the passage of the light through a large number of elements, all of which may be recognised by the lines they produce. The following are the wave lengths and position of the principal lines of the spectrum, the letters having been given in order to distinguish them:

<i>Absorption Line.</i>	<i>Wave Length.</i>	<i>Position in Spectrum.</i>
A'	$7,677 \times 10^{-8}$ cms. sec.	Red.
B	$6,870 \times 10^{-8}$ "	"
C	$6,563 \times 10^{-8}$ "	"
D	$5,893 \times 10^{-8}$ "	Yellow.
E	$5,271 \times 10^{-8}$ "	Green.
F	$4,862 \times 10^{-8}$ "	"
G	$4,341 \times 10^{-8}$	Purple.

The **D** line is characteristic of the metal sodium, whilst the **C**, **F**, and **G'** are lines in the hydrogen spectrum. The particular line for which the refractive index is measured is always denoted, the **D** line being generally taken and the refractive index then denoted by n_D .

In the manufacture of lenses and optical instruments, the refractive index is of vital importance. The focal length (f) of a lens is determined

by the curvature of the lens surfaces and the refractive index of the glass, and is given by the expression:

$$\frac{1}{f} = (\eta - 1) \left(\frac{1}{R_1} - \frac{1}{R_2} \right)$$

where R_1 and R_2 are the radii of curvature of the faces of the lens.

The great development in the manufacture of optical instruments of recent years has resulted in a number of investigations into the relationship between refractive index and composition, in order to increase the material at the disposal of the instrument maker.

A large amount of work was performed at Jena by Schott and Abbe, work which resulted in the introduction of a large number of new types of glass. More recently Peddle* has published the results of a systematic investigation of the variation of refractive index with composition in the case of the alkali (soda and potash), lime, lead oxide, and barium oxide, silica glasses. His method was to take series of glasses of the molecular types 100 SiO_2 , 20 R_2O , $x\text{RO}$ and 100 SiO_2 , 40 R_2O , $x\text{RO}$, where x was varied from 5 to 40 molecules, from which the variation of composition with varying calcium, lead, or barium content could be observed.

The extreme range over which η_D varies for glass is about 1.40 to 1.80.

(40) **Dispersion.**—The amount by which a spectrum is spread by a prism composed of a particular glass is dependent upon the relative refractive indices of the glass for rays at the opposite ends of the spectrum and the amount by which the spectrum is spread is called the total *dispersion*. Since this would be difficult to measure, the partial dispersions between particular lines, $\eta_C - \eta_D$, $\eta_D - \eta_E$, $\eta_E - \eta_F$, and $\eta_F - \eta_G$, are measured, whilst the dispersion $\eta_C - \eta_F$ is known as the mean dispersion. The ratio between the refractive index and the dispersion of a glass is expressed by the ratio $\frac{\eta_D - 1}{\eta_F - \eta_C}$, and is indicated by the Greek letter ν , a value, as we shall see, of importance in building up optical systems.

The focal length of a lens varies with the light by which the focus is obtained, the values for the **C** and **F** lines for the same lens being—

$$\frac{1}{f_C} = (\eta_C - 1) \left(\frac{1}{R_1} - \frac{1}{R_2} \right) \text{ and } \frac{1}{f_F} = (\eta_F - 1) \left(\frac{1}{R_1} - \frac{1}{R_2} \right) \text{ respectively.}$$

As a result, simple lenses give a series of images of varying colours, not quite superimposed, a phenomenon known as *chromatic aberration*, and it is evidenced by the coloured fringes which surround images given by such lenses. If two lenses be used together which possess varying ratios of refractive index to dispersion, it is possible to neutralise the dispersion of the first by means of the second without neutralising its refraction, the pair acting as a single lens free from chromatic aberration, and known as an *achromatic combination*. Until the work of Abbe and Schott, all known optical glasses had values of dispersion which varied proportionally with refractive index, and it was not possible to obtain a combination which destroyed chromatic aberration without neutralising

* J. Soc. Glass Tech., 1920, 4, 3, et seq.

the essential refractive power of the lenses. The Jena investigators, by widening the scope of the glasses used, were able to produce a number of new glasses in which the value of ν varied widely. Perfect achromatism is only secured when the two glasses spread the whole of the spectrum to the same extent, a condition not easy to fulfil. Thus, for instance, alkali-lead oxide-silica glasses spread the spectrum towards the blue end far more than do alkali-calcium oxide-silica glasses. For this reason, in accurate optical work, it is necessary to know not only the ν value, but also the relative partial dispersions, and these are usually stated as a ratio of the mean dispersion, thus—

$$\frac{\eta_D - \eta_A}{\eta_F - \eta_D} \text{ or } \frac{D - A}{F - C} = \alpha, \quad \frac{\eta_F - \eta_D}{\eta_F - \eta_C} \text{ or } \frac{F - D}{F - C} = \beta, \text{ and } \frac{\eta_C' - \eta_F}{\eta_F - \eta_C} \text{ or } \frac{C' - F}{F - C} = \gamma.$$

The two lenses which are perfectly achromatised will have values of ν as widely divergent as possible, but values of α , β and γ which are identical with one another. The conditions are so stringent that Schott has only succeeded in producing one pair on a commercial scale, having closely agreeing partial dispersion ratios—namely, a *telescopic crown* and a *telescopic flint*. Several other manufacturers of lenses for microscopic work have succeeded in producing practically completely achromatic combinations, generally by use of more than two types of glass or of the mineral *fluorite*, the term “*apochromatic*” being given to such combinations.

(41) **The Relationship between Optical Properties and Composition.**—

Before the work of Abbe and Schott the only glass-forming oxides, the optical properties of which were understood, were silica and the oxides of sodium, potassium, calcium, boron, phosphorus and lead. It was known that refractive index and dispersion increased with increase of density, the heavy lead glasses having high values for the constants whilst the lime glasses possessed smaller values. The nomenclature adopted was that of “*flints*” for the lead glasses of high density and refractive index, and “*crowns*” for the lime glasses. The problems solved by the research were the provision of glasses of varying ν values and also of the production of flints and crowns with a more similar relative dispersion throughout the spectrum. In order to obtain the results, a number of new elements were introduced, of which the acidic radicle, fluorine, and the basic oxides lithium, magnesium, cadmium, zinc, barium, and aluminium may be cited. Barium oxide was found particularly valuable in producing glasses of high refractive index but low dispersion. Boric oxide was found to lengthen the red end of the spectrum relatively to the blue; fluorine, potassium, and sodium, the blue relatively to the red. Summarised, we may express their results as to the effect of the different metallic oxides as follows:

(1) The mean refractive indices of fused amorphous boric oxide, and fused silica, or of alkali silicate glass, are raised by the solution of metallic oxides.

(2) The increase is not proportional to the weight of the dissolved oxide.

Take, for instance, the increase of refractive index of boric oxide

($\eta = 1.462$) when to 100 parts of this are added either 40 parts of barium oxide or an equivalent weight of lithium, zinc or lead oxides:

	Li_2O .	ZnO .	BaO .	PbO .
Molecular weight	29.88	81.37	153.37	223.10
Increase of η_D in the third decimal place ..	77	93	114	248

(3) The increase of refractive index is not proportional to the increase of concentration of the oxide.

(4) Boric oxide in alkali silicate glass at first causes an increase of refractive index, but with above 15 per cent. of B_2O_3 the reverse is the case.

The work of Peddle, previously noted, furnished a much more systematic idea of the variation of optical properties with composition. The difficulty of making optical glass lies not only in recording the optical constants but in producing glass of sufficient durability, free from colour, and not subject to devitrification during the slow cooling requisite whilst annealing is carried out. In conclusion, it may be said that nowadays optical glasses embrace practically all other types of glass.

(42) **Nomenclature.**—The method at present adopted is to designate as "Flint" glasses those containing lead and having a large index of refraction and a low value of ν , whilst "Crown" glasses are those having a high value of ν . Four chief divisions are recognised, (1) crowns, (2) barium crowns, (3) barium flints, (4) flints. The crowns are further subdivided into hard, soft, and boro-silicate crowns. Subdivisions are also made according to density, but these are arbitrary and depend upon the choice of different manufacturers. In general, they approximate in the case of barium crowns, barium flints, and flints to (a) extra light, density below 3.0; (b) light, density 3.0 to 3.5; (c) dense, 3.5 to 3.8; (d) extra dense, above 3.8. Of the following tables, No. XVI. is taken from glasses

TABLE XVI.—SCHOTT'S GLASSES: VARIATION IN OPTICAL CONSTANTS.

<i>Description.</i>	η_D .	$\nu = \frac{\eta_D - 1}{\eta_F - \eta_C}$.	$\alpha = \frac{\eta_D - \eta_A}{\eta_F - \eta_C}$.	$\beta = \frac{\eta_F - \eta_D}{\eta_F - \eta_C}$.	$\gamma = \frac{\eta_A' - \eta_F}{\eta_F - \eta_C}$.	<i>Density.</i>
Borosilicate crown	1.4944	66.5	.667	.698	.554	2.33
Light silicate crown	1.5086	61.8	.643	.702	.564	2.46
Ordinary silicate crown	1.5175	59.0	.642	.702	.568	2.54
Heavy barium silicate crown	1.5726	57.5	.633	.706	.571	3.21
Heaviest baryta crown	1.6130	56.4	.629	.706	.576	3.60
Borosilicate flint	1.5503	49.4	.637	.706	.578	2.81
Baryta light flint	1.5646	55.4	.635	.706	.575	3.11
Baryta flint ..	1.6235	39.1	.605	.713	.604	3.67
Heavy baryta flint	1.6570	36.3	.604	.716	.611	3.95
Extra light flint ..	1.5473	45.9	.620	.710	.591	2.93
Ordinary light flint	1.5800	42.2	.616	.712	.602	3.22
Heavy silicate flint	1.6489	33.8	.600	.714	.615	3.87
Very heavy silicate flint	1.7782	26.5	.584	.721	.635	4.99

in Schott's catalogue and illustrates the variation of the optical constants in the different divisions (this firm lists more than ten types of crown glasses), whilst No. XVII. gives an idea of the varying compositions of the glasses used for optical work.

TABLE XVII.—COMPOSITIONS OF SOME OPTICAL GLASSES.*

Percentage Composition.								
	Light Flint.	Dense Flint.	Very Dense Flint.	Barium Flint.	Light Crown.	Boro-silicate Crown.	Dense Barium Crown.	Phosphate Crown.
SiO ₂ ..	53·9	39·0	20·0	53·69	68·5	68·2	39·6	(P ₂ O ₅) 70·5
PbO ..	36·7	49·0	79·9	16·71	—	—	3·0	—
K ₂ O ..	6·0	4·0	—	8·31	5·0	9·5	—	12·0
Na ₂ O ..	1·0	3·0	—	1·69	12·0	10·0	—	—
BaO ..	—	—	—	14·27	9·7	—	44·0	—
CaO ..	1·96	4·0	—	—	—	—	2·0	—
ZnO ..	—	—	—	2·68	1·0	2·0	7·7	—
B ₂ O ₃ ..	—	—	—	—	3·5	10·0	5·0	3·0
As ₂ O ₃ ..	0·3	0·2	0·1	2·53	0·2	0·2	0·4	0·5
Sb ₂ O ₃ ..	—	1·0	—	—	—	—	—	—
Al ₂ O ₃ ..	—	—	—	—	—	—	—	10·0
MgO ..	—	—	—	—	—	—	—	4·0
Mn ₂ O ₃ ..	—	—	—	—	—	0·06	—	—
η_D ..	1·5803	1·6068	1·6555	—	1·5179	—	1·5905	—
ν ..	41·0	37·5	34·4	—	60·9	—	57·0	—

Peddle has proposed a much more systematic nomenclature than at present used. He suggests the primary divisions (1) ordinary crowns, (2) zinc crowns, (3) fluor crowns, (4) phosphate crowns, (5) barium crowns, (6) barium flints, and (7) flints. The subdivision suggested is by refractive index and not by density, thus :

TABLE XVIII.—SUGGESTED CLASSIFICATION OF OPTICAL GLASSES (PEDDLE).

Ordinary Crowns.		Barium Crowns and Flints.		Flints.	
Name.	η_D .	Name.	η_D .	Name.	η_D .
Light ..	below 1·50	Light ..	below 1·56	Extra light	below 1·57
Medium ..	1·50 – 1·52	Medium ..	1·56 – 1·59	Light ..	1·57 – 1·60
Dense ..	above 1·52	Dense ..	1·59 – 1·63	Dense ..	1·60 – 1·64
		Extra dense	above 1·63	Extra dense	1·64 – 1·70
				Double extra dense	above 1·70

(43) **Absorption of Light.**—A beam of light passing through glass is always partly absorbed, and the absorption may be either fairly even

* THORPE'S Dictionary of Applied Chemistry.

throughout the spectrum, producing a glass which is practically colourless when the absorption is small, and grey when it is appreciable, or there may be pronounced selective absorption produced by the presence of coloured salts or by colloidal solutions. The amount of light absorbed is proportional to the thickness of the glass. In the case of glass made from pure materials and practically free from colour, such as the best optical glass, the total absorption is small, not amounting to more than 1 or 2 per cent. of the incident light. Unpolished mirror glass of a thickness of 8 millimetres may absorb 13 per cent. of the light. The *selective absorption* of coloured glass has been studied by Zsigmondy,* who, to twelve glasses of widely differing type, added known amounts of the oxides of copper, manganese, iron, cobalt, uranium, nickel, and chromium, and examined the absorption produced over the range of the

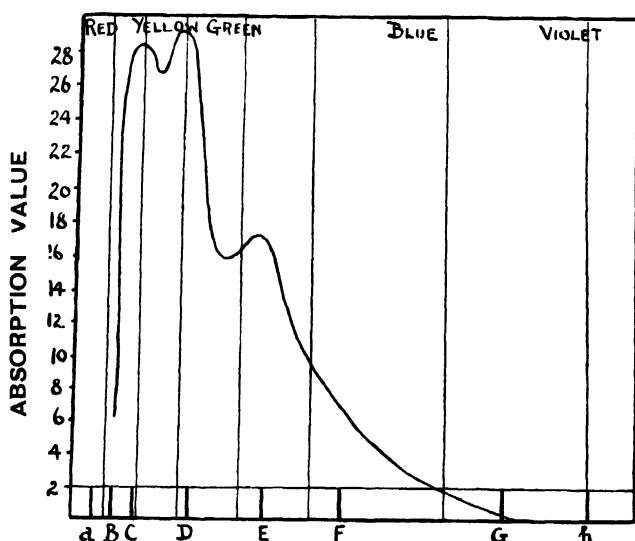


FIG. 5.—ZSIGMONDY'S CURVE ILLUSTRATING THE SELECTIVE ABSORPTION OF COBALT GLASSES.

spectrum. The amount of absorption and the consequent colouring power were found to vary largely with the oxides examined, and in the case of the same oxides the effect was dependent upon the composition of the glass itself and also upon the concentration of the colouring compound. Uncertainty as to the state of oxidation, particularly in the case of iron, manganese, and chromium, weakens the value of the results obtained, for variation of the valency of the metals alters the colour of the salts which they produce. A reproduction of his curve for cobalt glass is given in Fig. 5.

Absorption is dependent upon increase of temperature, which generally produces increased absorption, whilst the absorption bands either remain stationary or move towards the red end of the spectrum, returning usually

* *Ann. d. Phys.*, 1901, 4, 60

to their previous positions on cooling. The following table (Table XIX.) illustrates the relative transmission factors at different temperatures.

TABLE XIX.—RELATIVE TRANSMISSION FACTORS AT DIFFERENT TEMPERATURES.

Colouring Agent.	Colour.		Relative Transmission Factor.		
	Cold.	Hot.	30° C.	200° C.	350° C.
Cobalt	{ Light blue	—	100	104	108
	{ Deep violet	Deep blue	No appreciable change		
Gold	{ Pink	Violet	100	96	93
	{ Deep red	—	100	67	42
Copper	{ Medium red	—	100	92	84
	{ Bluish green	Yellowish green	100	94	82
Manganese ..	{ Purple	Bluish violet	100	94	90
Chromium ..	{ Yellowish green	Yellow	100	84	67

Gibson* found that a glass coloured by selenium and cadmium was yellow at 180° C., orange at the ordinary temperature, and bright red at 430° C., whilst a zinc silicate glass coloured by the same agents changed from a bright red to a very deep red over the same range. Not only is knowledge of the transmission of visible light waves important, but in some cases it is necessary to study the transmission of rays beyond limits of the visible spectrum. *Ultra violet rays* are extremely active in promoting many chemical changes, a proof of which is given by their action upon the photographic plate. Ordinary types of glass are practically impervious to ultra violet rays, and the microscopic and telescopic systems made from special glasses which transmit light beyond the visible violet are much more effective for photographic purposes than ordinary lens systems. Schott and Gen. of Jena have produced special glasses fairly transparent to ultra-violet rays from which they have been able to construct an *astro-photographic objective* which increased the number of stars recorded in the ratio of 3 to 2.

Fused quartz and boric oxide are transparent to ultra-violet radiation; a fused mixture of boric oxide, fluorspar, and alumina shows only a weak absorption, whilst lead glasses are strongly absorbent. Glasses coloured by nickel, in the absence of appreciable quantities of lime, magnesia, lead oxide, alumina, and boric oxide, are stated to give high transmission of ultra-violet light, whilst absorbing visible light. For medical purposes vitreous (not crystalline) silica is used to make tubes for mercury vapour lamps for producing light beyond the visible violet, but at present only small vitreous silica lenses of sufficient freedom from bubbles can be provided for optical purposes. Glass varies with varying composition in its transmission of X-rays. A lithium glass, for instance, is much more permeable than a soda glass.

The transparency of glass to heat rays is dependent on the com-

* *Phys. Rev.*, 1916, [ii], 7, 194.

position of the glass. Zsigmondy prepared a glass of high ferrous oxide content, which at a thickness of 8 millimetres completely absorbed all heat rays, whilst Crookes, by using a soda lime batch containing 10 per cent. of ferrous oxalate, obtained a glass which absorbed 98 per cent. of the heat radiations. Ferroso-ferric oxide (Fe_3O_4) along with the mineral *biotite* in a soda-lime glass is also effective in cutting off heat rays. Other oxides producing the same effect are those of cerium, chromium, and titanium.

Sherwood found that a soda lime batch containing some borax and the oxides of manganese, titanium and nickel, along with an artificial *biotite*, gave the best structural heat-resisting glass (see Structural Glass). Oxidising conditions were needed for melting the glass.

Plate glass, so prepared, transmitted a total of 77 per cent. of the light rays but only 22 per cent. of the heat rays.

CHAPTER V

THE VISCOSITY OF GLASS AND ANNEALING

(44) **Definition of Viscosity.**—When a liquid flows over a horizontal solid surface, the layer of liquid next the solid is at rest owing to cohesion between the particles of liquid and solid, and successive horizontal liquid layers move with successively increasing velocities. Each layer of liquid exerts a force upon the more rapidly moving layer above it, tending to retard motion, the force being due to a kind of friction between the particles of the two layers, termed the *viscosity* of the liquid. Viscosity varies greatly in different liquids, it is dependent upon their constitution, and, for the same liquid, the viscosity varies with the temperature. Glycerine is a more viscous liquid than water at the same temperature, whilst hot glycerine is less viscous than cold glycerine.

(45) **Methods of Measuring Viscosity.**—In the case of liquids which can be made to flow through a long narrow tube (of length l and radius of bore r) when subjected to a pressure p , the volume V flowing per second, according to Poiseuille, is related to the viscosity η by the equation $V = \frac{\pi p r^4}{8l\eta}$. If the same tube is used and different liquids are subjected to the same head of pressure, the volumes passing per second are inversely proportional to the viscosities. For substances which liquefy only at high temperatures the simple flow method for determining the viscosity cannot be used. In such cases Margules confined the liquid between two concentric cylinders, of which the outer one revolved at a constant speed. A torque was thus exerted upon the inner cylinder of a value proportional to the viscosity of the intervening liquid, and this was measured. Washburn* stirred liquid glass with a porcelain rod driven by a motor, determined the power consumption due to the stirring, and the angular velocity of the rod, data allowing of the calculation of the viscosity of the glass.

Masson, Gilbert, and Buckley† suggest the method of determining the rate of fall of a metal sphere through the liquid, by means of X-ray photographs at regular intervals, whereby, from a law due to Stokes, the viscosity of the liquid can be calculated.

(46) **The Effect of Temperature on Viscosity.**—The variation of viscosity with temperature is strikingly illustrated in the case of glass; ordinary soda-lime glass, for instance, is fairly fluid at temperatures of about 1400°C ., but the viscosity rapidly increases as the glass cools until,

* *J. Amer. Cer. Soc.*, 1920, **3**, 735.

† *J. Soc. Glass Tech.*, 1921, **5**, 337.

in general, the glass is highly viscous at 1000°C . At lower temperatures still, the viscosity becomes so great that no flow is possible, and the glass becomes rigid. The point is well illustrated by the viscosity-temperature curve of a glass having the composition:

SiO_2	72.0	per cent.
CaO	5.5	"
Al_2O_3	3.0	"
Na_2O	15.0	"
K_2O	4.5	"

the curve (Fig. 6) being due to K. Arndt.* It will be seen how material a factor upon viscosity is the temperature, a change from 1300°C . to 1000°C . causing roughly a tenfold viscosity increase.

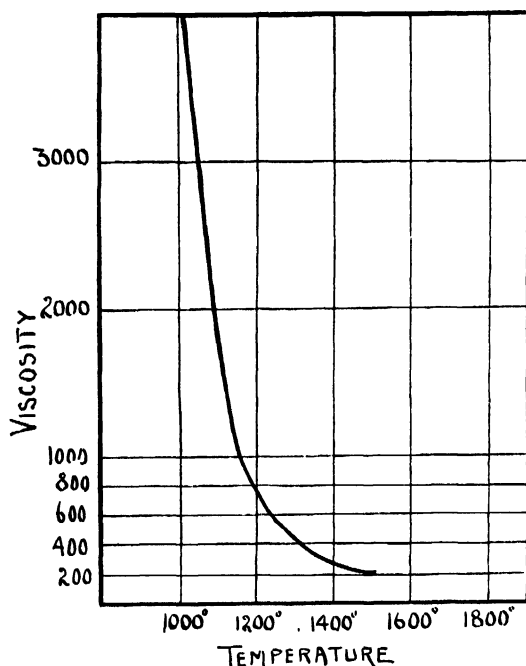


FIG. 6.—A TEMPERATURE-VISCOSITY CURVE DUE TO K. ARNDT.

For successful working, glass must be sufficiently fluid at the furnace temperature to allow of complete founding. If it is too viscous, the small gas bubbles cannot escape and seedy metal is obtained. Where the glass is delivered by a flow device it will need to have a lower viscosity than when hand gathered, and in the latter case, the temperature after fining must be substantially lowered before the glass can be worked.

The metal also must have a rate of increase of viscosity with decrease of temperature, in other words a viscosity range, or a rate of setting,

* *Zeitsch. Chem. Apparatenkunde*, 1908, 3, 474

suitable for the treatment which it receives during working. Glasses undergoing a working process consisting of several stages must have, in general, a longer viscosity range than those which are rapidly shaped after gathering. Hand-blown bottles must stiffen rapidly in the mould, and quick-setting glass is the best type for hand working; on the other hand, bottles made by rapid automatic machinery where several processes are entailed (*i.e.*, pressing and blowing), and where the glass is rapidly chilled by coming into contact with large masses of metal, are best made from slow-setting glass.

(47) **The Effect of Composition on Viscosity.**—We possess little systematic knowledge of the effect of the individual glass-forming oxides upon the viscosity of glass, most of the data at present known being of the nature of qualitative comparisons. Feild,* using a modification of Margules' method, has determined the actual viscosities of blast furnace slags, which, whilst not resembling simple glasses, yet are composed of some of the oxides most common in glass—namely, silica, lime, alumina, and magnesia—and his results have given an invaluable indication of the effect of the oxides in question. The following list indicates the viscosity effects of the common glass-making oxides.

SILICA.—Other things being equal, increase of silica results in an increase of viscosity in all types of glass. The intensity of its effect depends upon the relative amounts of the other constituents of the batch. Generally speaking, highly siliceous glasses have a long viscosity range.

LIME.—If lime is substituted for soda in batches, the silica being maintained constant, the viscosity of the glasses produced increases with the increase of lime content. Similarly, an increase in the rate of setting occurs. When, however, the proportion of lime is increased relatively to those of silica and soda, beyond a certain limit, a rapid decrease of viscosity takes place. A glass made from the following batch, sand 40, limestone 100, soda-ash 20, melted in a three-pound crucible in twenty minutes at 1350° C., poured out like oil, and set almost instantaneously. Increase of lime tends invariably to increase the rate of setting. It may be said that soda-lime glasses with a proportion of lime up to about 10 or 12 per cent. are quite viscous at temperatures below 1300°, but are exceedingly fluid above 1350°.

BORIC OXIDE.—This substance causes a pronounced reduction of viscosity.

SODIUM OXIDE.—Addition of sodium oxide causes a reduction of viscosity and produces a long viscosity range.

POTASSIUM OXIDE.—Potassium oxide is similar to sodium oxide in its action, but it is less effective, weight for weight. An equimolecular mixture of soda and potash gives viscosity phenomena intermediate between those of the two oxides alone. Littleton and Roberts† assumed that the rate of annealing of glass was proportional to its viscosity, and for a glass of known annealing point determined the viscosity at that point, applying the value obtained to find the annealing point of other glasses. They found the assumption to be justified in practice.

* *Trans. Faraday Soc.*, 1917, 13, 3.

† *J. Opt. Soc. Amer.*, 1920, 4, 224.

ALUMINA.—Increase of alumina generally increases the viscosity of the glass more rapidly than increase of silica, but it also increases the viscosity range. Small amounts of alumina added to a viscous lime-containing glass cause, however, a reduction of viscosity.

MAGNESIA.—This oxide is somewhat similar in effect to lime, though in amounts up to 9 or 10 per cent. it does not increase the viscosity to the same extent, whilst beyond this point no decrease of viscosity is obtained as in the case of lime. High magnesia glasses become cordy, ragged, and stringy and appear to be very viscous on account of this. In general, it may be said that magnesia glasses do not become so fluid at high temperatures as lime glasses, whilst they set less quickly since they have a longer viscosity range. A small quantity of magnesia added to a viscous lime glass causes a very pronounced reduction of viscosity.

LEAD OXIDE.—The presence of lead oxide in a glass reduces the viscosity and lengthens the viscosity range very considerably.

(48) **Softening Temperature.**—Although no definite melting point is obtained for glass, the range over which particular glasses soften is well defined. The following oxides lower the softening temperature: boric oxide, phosphoric oxide, lead oxide, baryta, soda, potash, iron oxide, and manganese oxide. On the other hand, the tendency of silica, lime, and alumina is to give, in general, a high softening point.

Softening temperatures lie between 400° C. and 800° C. An example of a glass with a fairly high softening point is Bohemian crystal, a potash-lime glass, rich in silica, whilst lead glasses are softened at comparatively low temperatures.

(49) **Surface Tension.**—The surface of any liquid acts as if it were covered by an elastic skin, due to internal molecular attraction, and the force at the surface is called the surface tension of the liquid. The fining of glass is dependent upon the surface tension as well as upon the viscosity of the liquid.

Griffith* found the surface tension of glass to be an approximately linear function of the temperature. For a glass of the composition SiO_2 69.2 per cent.; K_2O 12 per cent.; Na_2O 0.9 per cent.; Al_2O_3 11.8 per cent.; CaO 4.5 per cent.; MnO 0.9 per cent., he obtained the following values:

<i>Temperature.</i>	<i>Surface Tension (Lbs. per Inch).</i>	<i>Temperature.</i>	<i>Surface Tension (Lbs. per Inch).</i>
1,100°	0.00230	801°	0.00257
852°	0.00249	745°	0.00251

The Annealing of Glass.

(50) **The Polarisation of Light.**—We have pointed out that glass when cooled rapidly becomes strained, and gives different values for many physical properties from those obtained from the same glass which has been cooled down very slowly, or, as we say, that has been annealed.

The fact that glass is strained is very conveniently shown by the use of polarised light—a method due to Brewster. It is found that strained

* *Phil. Trans.*, 1920, 220, A, 587.

glass turns the plane of vibration (or polarisation) of plane polarised light which passes through it. Normally, light consists of vibrations in the ether in directions at right angles to that of the path of the rays. Suppose point **O** (Fig. 7) to be a point situated in the path of a ray of light passing at right angles to the plane of the paper. For an unpolarised ray, point **O** will vibrate in any direction in the plane of the paper, since this is at right angles to the direction of the ray, and **AOB**, **COD**, **EOF** may all represent the path of the vibrating point. Where light is polarised the vibration of **O** will only be in one particular direction, such, for instance, as **AOB**, or in other words, the light ray will be polarised along a plane through **AB** at right angles to the paper. Polarised light may be obtained by the suitable reflection of ordinary light at a glass surface, or by passing the light through a *Nicol prism*, which consists of two pieces of Iceland spar crystals specially cut and cemented together. Imagine a ray of light to be polarised along a plane through **AB** by passing through a nicol prism, and then passed through a second nicol prism with its polarising plane parallel to the first. It is evident in this case, that the whole of the ray which has passed the first prism will traverse

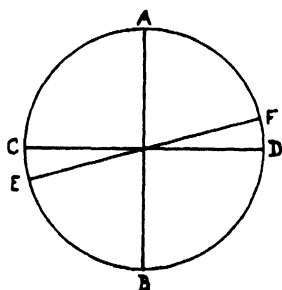
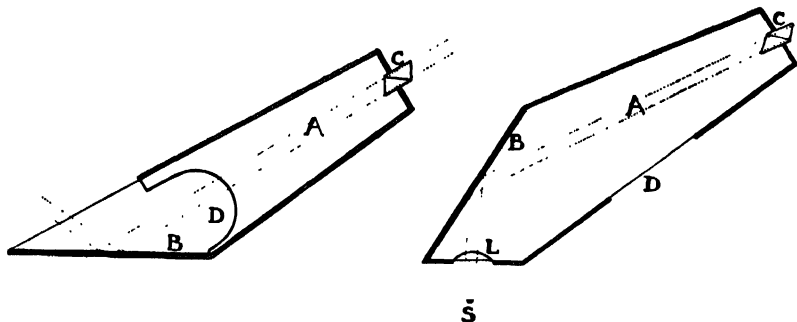


FIG. 7.—THE POLARISING OF LIGHT.

the second. Where the second nicol has its plane of polarisation at right angles to the first (as along **CD**) it will cut off all the light from the first nicol and total darkness will result, the nicols being said to be "crossed." Consider a piece of strained glass placed between two crossed nicol prisms, then, since strained glass has the power of rotating the plane of polarisation, the light will not be polarised in a direction at right angles to the plane of the second prism on emerging from the glass. To make the point clearer, take **AB** and **CD** (Fig. 7) as the polarisation planes of the first and second of the two nicols in question. The direction of vibration of the ray of light on emerging from the strained glass will not be along **AB** but in some other direction, such, for instance, as **EF**. Now the ray with its polarisation plane along **EF** can partially pass through the nicol with its polarising plane along **CD**, and the nearer **EF** coincides with **CD** the more the light which can pass the second nicol prism. The amount to which the plane of polarisation is turned by the glass depends upon the degree of strain, so that with increasing strain **EF** more nearly approaches **CD**, and the greater is the amount of light passing through the second nicol.

(51) **Strain Testers.**—An instrument of this type is extremely useful in examining glass for strain, and several "strain testers" are on the market. The design of the instruments is as follows: a beam of light from a suitable source is passed through a lens, to render the rays parallel, and is then polarised either by passage through a nicol prism or reflection from a series of plates of glass laid upon one another and set at a definite angle to the ray of light. The ray from the polariser is examined through a small nicol, called the *analyser*. The analyser is first rotated until the field is dark (the nicols then being "crossed") and the glass to be ex-

examined is afterwards placed between polariser and analyser with its long axis at an angle of 45° to the plane of polarisation of the analyser. Where strain occurs, the field is bright, all unstrained portions remaining dark.



FIGS. 8 AND 9.—THE "ENGLISH" STRAIN FINDER.

Apparatus of the kind described have been devised by Messrs. Adam Hilger, Ltd., London,* G. V. Wilson,† and S. English.‡ Such instruments can be used for examining glass in order to detect the presence of strain,



FIG. 10.—THE APPEARANCE OF THE END OF A STRAINED GLASS ROD VIEWED THROUGH NICOL PRISMS.

(Seven Rings and Cross).

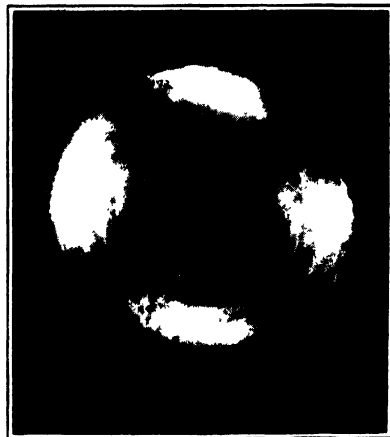


FIG. 11.—THE APPEARANCE OF A PARTIALLY ANNEALED GLASS ROD VIEWED THROUGH NICOL PRISMS.

(Diffuse Cross only).

and are applicable to all types of glass which are transparent to light. Dark green, dark amber or black glass obviously cannot be tested in such a manner.

* *J. Soc. Glass Tech.*, 1919, 3, 256.

† *Ibid.*, 1919, 3, 258.

‡ *Ibid.*, 1917, 1, 61.

One form of the "English" strain viewer, for use with daylight, consists of a wooden box **A** (Fig. 8), painted dull black inside, the bottom **B** being a sheet of plate glass or preferably several layers of sheet glass. Light reflected from this glass is polarised, and it is examined through a nicol prism **C** fixed in the small end of the box. The article to be examined is held in position through an opening **D**. Fig. 9 represents the plan view of a form for use with artificial light. The polarising glass **B** here stands vertically, and a lens **L** is introduced for rendering parallel the beam of light.

(52) **The Effect of Heat on Strained Glass.**—Fig. 10* gives the photograph of a typically strained rod of glass viewed through a strain tester, in which case there is seen to be a dark cross and a series of concentric coloured rings about the central axis of the rod. The effect of heat upon unannealed glass can be very beautifully shown by heating a

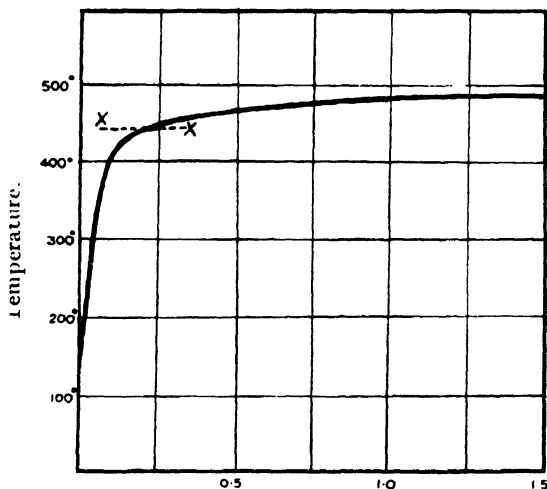


FIG. 12.—THE RATE OF BENDING OF GLASS ROD.
Bending—> X—Upper Annealing Temperature.

portion of glass rod in an electric furnace placed between the nicols of a strain tester. With gradually increasing temperature no change is visible over a range of several hundred degrees, but, at a temperature which depends upon the composition of the glass, and is usually between 450°C. and 600°C. , the rings begin slowly to expand and then to disappear, until only the black cross is visible (see Fig. 11).* Then, as annealing proceeds, the cross becomes more diffuse and spreads over the field until complete darkness results and the glass is free from strain. At the lowest temperature at which strain is removed, named the **lower annealing temperature**, the rate of annealing is extremely slow and takes days to complete. By heating the rod above this point the rate of annealing becomes more and more rapid, until at a temperature

* ENGLISH and TURNER, *J. Soc. Glass Tech.*, 1918, 2, 90.

some 150° C. or so above the lower annealing point strain is removed exceedingly rapidly, whilst a temperature is finally reached above which no residual strain is possible, a point known as the **upper annealing temperature**. The figures below, obtained by English and Turner,* represent the time taken for a rod of "chemical" glass to anneal at the temperatures given, 500° C. being the lower and 630° C. the upper annealing temperature.

<i>Temperature.</i>				<i>Time Required to Anneal.</i>
500°	?
550°	Not completed after 9.5 hours.
600°	4.5 hours.
625°	18 minutes.
630°	10 "

Between 600° C. and 630° C. each rise of 7° C. roughly halved the time taken for annealing.

The temperature usually termed "annealing temperature," corresponds to this upper annealing temperature, and has been defined by Twyman† as that temperature at which 95 per cent. of the original stress in the glass is removed within three minutes.

(53) **The Softening of Glass over the Annealing Range.**—It can be readily shown that when glass reaches the neighbourhood of the upper annealing temperature it becomes much softer than when it is at lower temperatures, and it will be evident that it is because of the softening of the glass that strains can be removed. A simple method of indicating the softening has been described by English and Turner.‡ A rod of glass held horizontally at one end was placed in an electric tube furnace, the temperature of which was raised at a definite rate. The rate of softening was measured by the rate at which the rod bent, a pointer attached to the free end of the rod passing over a scale. The rate of bending was found to be small but slowly increasing until the upper annealing temperature was approached, when a fairly sudden change took place and the rate of bending became much more rapid. By plotting a curve with temperatures as ordinates and rates of bending as abscissæ (see Fig. 12), it was found possible to indicate roughly the upper limit of the annealing range. Littleton and Roberts§ have given a variation of the method in which the free end of the rod was subjected to a shearing couple by means of a pulley, and the rate at which the pulley rotated at various temperatures was noted.

(54) **The Rate of Expansion of Glass over the Annealing Range.**—Peters and Cragoe|| and also Pietenpol¶ have shown that the rate of expansion of annealed glass is linear at all temperatures up to the lower annealing point, when a sudden increase in the rate occurs which lasts over the whole annealing range. Beyond the upper annealing temperature the rate again decreases, the two former workers stating that a contraction here occurs, but Pietenpol claims that there is a small rate of expansion in this region. For unannealed glass the rate of expansion

* ENGLISH and TURNER, *J. Soc. Glass Tech.*, 1918, 2, 90.

† *J. Soc. Glass Tech.*, 1917, 1, 70.

‡ *J. Opt. Soc. Amer.*, 1920, 4, 224.

¶ *Chem. and Met. Eng.*, 1920, 23, 876.

§ *Loc. cit.*

|| *Ibid.*, 1920, 4, 105.

at first is greater than that for unstrained glass, but just below the annealing range Pietsenpol found that the rate decreased until it coincided with that of the annealed glass in the annealing range, the originally strained sample then acting exactly as an annealed glass.

(55) **The Conditions for the Successful Annealing of Glass.**—By maintaining glass at its upper annealing temperature, strain is rapidly removed, but the success of the annealing of glassware depends upon cooling the glass without any reappearance of strain. When the rate of cooling is extremely slow the temperature of the glass can remain uniform throughout the mass, and no strain will result; but rapid cooling tends to give a badly annealed glass. Over what temperature range must the rate of cooling remain slow? In practice the rate varies with the different methods employed. In lehrs there is a regular fall from the hot to the

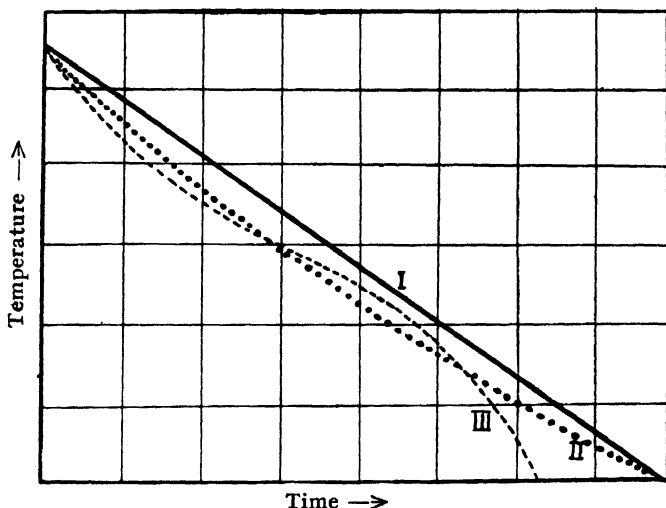


FIG. 13.—ANNEALING CURVES FOR GLASS.

cold condition. In kilns the rate of cooling becomes slower as the temperature falls. English and Turner* have come to the conclusion, based upon many observations, that, in the upper part of the annealing range, cooling can be fairly rapid, as will also be the case below the lower annealing point, when the glass has completely set, and is rigid enough to withstand forces which tend to cause strain. The point of danger is in the lower part of the annealing range where stiffening of the glass is rapidly taking place. Consequently the temperature-time curve of annealing must be of the type III. (Fig. 13), curve I. representing the cooling rate in lehrs and curve II. that in kilns. As an illustration they state that a glass with an upper annealing temperature about 585°C. or 590°C. could be cooled at a rate of 25°C. per hour from 590°C. to 500°C. , but even a reduction to 9°C. per hour over the range

* *Loc. cit.*

500° C. to 400° C. resulted in the production of a very slight strain. Whatmough* has applied the conclusions of English and Turner in building a small annealing lehr for articles made from glass tubing. The lehr consists of a central gas muffle, a short entrance limb, and a long exit or cooling limb. Temperatures along the tube are regulated by the adjustment of the heating burners, and by controlling the rate of heat lost along the exit limb, the sides of which consist of metal plates lagged with slag wool in suitably adjusted amounts along the tube. Further regulation is obtained by removing some of the gases at any suitable point along the cooling limb. Records from a series of thermocouples allow of arrangement of the rate of cooling along the lehr. Extremely successful results have been obtained by the method.

(56) **The Relationship between the Annealing Temperature and the Chemical Composition.**—The two chief data in annealing are (1) the upper annealing temperature which is the temperature peak in the lehr, and (2) the rate of cooling of the glass necessary to prevent strain in the glass. Observations upon these points are very scanty, the only systematic work having been carried out by English and Turner.† Summarised, their results are as follows:

(a) **SODA-LIME AND SIMILAR GLASSES.**—The annealing temperatures of a number of soda-lime glasses are given in Table XX.

TABLE XX.—ANNEALING TEMPERATURES OF SODA-LIME GLASSES.

Glass.	Percentage Composition			Upper Annealing Temperature.
	SiO ₂ .	Na ₂ O.	CaO.	Degrees Centigrade.
3	74·08	23·00	2·61	492 ¹
5	73·78	20·78	4·50	512
7	74·41	17·20	7·45	538
9	74·96	14·88	9·36	562
11	74·93	13·02	11·68	601
17	69·73	11·22	17·38	613

Other oxides—MgO, Al₂O₃, Fe₂O₃, As₂O₅—were present in the above glasses, but only in small amounts (below 0·6 per cent.).

The first five glasses which were members of a series of approximately constant silica content showed a regular rise of annealing point as lime replaced soda. The figures proved that glasses rich in alkali can be annealed at fairly low temperatures. Glasses 7 and 9 are of the type usually used for ordinary white flint gla's, for medical, paste, and sauce bottles, and for those used in machines with automatic feeding devices. Glass 17 is a type of high lime product used for bottles made by the hand process. The lower limit of the annealing range of glass of composition approaching No. 7 is about 320° C., and in practice, rod of 7·4 mm. diameter was found to require 3·5 hours to cool from 550° C. to 320° C.

* *J. Soc. Glass Tech.*, 1921, 5, 44.† *Loc. cit.*

to obtain it reasonably strain-free, whilst the cooling from 320° C. to the normal could be carried out in 3 hours.

As compared with lime, alumina was found, in general, to reduce the annealing temperature of glass.

Soda-magnesia glasses were found to have lower annealing temperatures than soda-lime glasses of the same molecular composition, from which the inference was drawn that, over the range studied (soda-lime glasses 3 to 11 above), substitution of dolomite for some or the whole of the limestone facilitated annealing.

(b) LEAD GLASSES.—Glassware containing lead oxide has a low annealing temperature. Three glasses varying in composition over the range SiO_2 , 57 to 64 per cent., PbO , 17 to 30 per cent., alkali, 11 to 15 per cent., had annealing points at 450° C. to 460° C. A rod 7 mm. in diameter could be cooled from 450° C. to 400° C. at 120° C. per hour, from 400° C. to 300° C. at only 50° C. per hour, and below 300° C. at 300° C. per hour. Electric lamp globes of lead glass could be cooled at 12° C. per minute between 450° C. and 300° C., and could be brought into the open air below the latter temperature.

(c) GLASSWARE OF COMPLEX COMPOSITION.—Complex chemical glassware was found to be the most difficult to anneal of all the types examined. A glass of the composition:

SiO_2	64	per cent.
Al_2O_3	10	„
CaO	7	„
B_2O_3	7	„
Na_2O and K_2O	11.5	„

was annealed at 630° C. and between 500° C. and 400° C. needed such slow cooling that an 8 mm. rod always showed sign of strain.

A lamp glass of the composition:

SiO_2	65	per cent.
B_2O_3	23	„
Al_2O_3	2	„
Na_2O and K_2O	10	„

annealed at 585° C. to 590° C., and cooling of a rod 6.25 mm. in diameter could not be carried out at above 9° C. per hour between 500° C. and 360° C.

A soft soda glass, such as is used for lamp-working, annealed at 530° C.

APPENDIX.

S. English has recently (1924) measured the viscosity of many types of glass from the annealing temperatures to 1400° C. At lower temperatures he measured the rate of extension of standard-sized rods under definite loads; at higher temperatures he employed a method involving the rotation of a platinum cylinder in a cylindrical vessel containing molten glass. As an example, the figures below are extracted from results for a soda-lime-silica glass of the percentage composition SiO_2 75.0, CaO 8.2, Na_2O 16.0:—550° C. $\eta = 3.33 \times 10^{12}$; 600°, 6.67×10^{10} ; 650°, 3.82×10^9 ; 700°, 2.80×10^8 ; 749°, 1.00×10^7 ; 798°, 1.41×10^6 ; 900°, 4.75×10^4 ; 1002°, 6.34×10^3 ; 1094°, 1.82×10^3 ; 1205°, 5.84×10^2 ; 1300°, 2.36×10^2 ; 1392°, 1.54×10^2 .

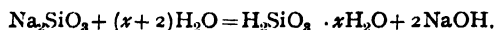
CHAPTER VI

THE DURABILITY OF GLASS

(57) **The Necessity for High Durability of Glass.**—Of great importance amongst the properties of glassware is its power to withstand the action of decomposing and disintegrating agents. Glass used for containers is often subjected for long periods to the action of the liquid it holds—which may be neutral, acid, or alkaline in character. It is important that no material amount of the glass should dissolve in the liquid—particularly where the vessels contain medicines, foods, or beverages. The stability of chemical glassware is also of great importance, for it is quite possible for poor glassware to vitiate delicate estimations. For instance, a flask or vessel of soft soda-lime glass in which water is boiled, will liberate so much alkali in 15 minutes as to make impossible correct titrations with decinormal solutions. Again, many years ago chemists, such as Berzelius and Stas, found that precipitates obtained in glass vessels were likely to be contaminated with silica, or, when acids had been used, with salts due to the attack of the acids upon the glass. Ordinary containers do not need to be as resistant as chemical glassware, and whereas good soda-lime glass is quite suitable for most vessels in which liquids are held, it has been necessary to seek for fresh types of glass, from which to create vessels for use in chemical manipulation. Another source of attack to be considered is the weathering which occurs in the case of glass exposed to the atmosphere—where moisture and gases such as carbon dioxide occur—whilst in the case of glass used in towns small amounts of ammonia, sulphuretted hydrogen, sulphurous and sulphuric acids are found in the atmosphere. With window and similar types of glass, attack results, after more or less prolonged exposure, in roughening of the surface, and in the production of an iridescent or opalescent coating on the exposed face. With optical glass, atmospheric weathering is of extremely great importance, for the slight filming of lenses is often disastrous in its results on expensive and delicate optical combinations, whilst the subject is further complicated in that, in order to obtain the correct optical factors of refractive index and dispersion, glass of relatively poor chemical stability has sometimes to be used.

(58) **The Nature of the Weathering and Chemical Attack.**—Moisture, in contact with glass, is first of all adsorbed and then absorbed. The resulting hydration is succeeded by the hydrolysis of the soluble silicates forming part of the complex silicate mixture of which glass consists. In a soda-lime glass sodium meta-silicate is the most soluble silicate

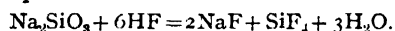
present and hydrolysis chiefly results in the liberation of sodium hydroxide and silicic acid according to the equation:



The caustic soda passes into solution, whilst the silicic acid (which contains an uncertain number of molecules of water of hydration) is also to some extent soluble, and again is partly mechanically removed, often giving the water a turbid appearance. The action of the water is not always a surface one, for it can be shown that, in many cases, it penetrates to an appreciable depth below the surface, which, on subsequent drying and heating, shows a large number of minute cracks and causes the glass to present a dull appearance. Under similar conditions to those used for the aqueous attack, much larger amounts of material are removed by the action of the alkalis, caustic soda, and sodium carbonate, than when the surfaces are subjected to attack by water alone. The reaction is roughly parallel to that of water upon the various types of glass, samples, in general, badly attacked by water being also badly attacked by alkalis. Of the acids, concentrated sulphuric acid has very little action upon glass, whilst dilute acids usually are very similar to water in their effect, and indeed probably derive their action from the water present. Concentrated hydrochloric acid is selective in its action, and some glasses are fairly strongly attacked by it.

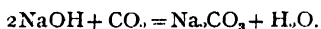
The action in all cases is largely dependent upon temperature, and whereas, at normal temperatures, the amount of material removed is slight, it increases rapidly when higher temperatures are reached. A glass which was found to lose an inappreciable amount per square decimetre when subjected to the attack of 2-normal caustic soda* for 3 hours, lost 4.1 milligrams at 60° C., 18.9 milligrams at 80° C., and 74.2 milligrams at 100° C.†

In quite a different category to the attack of other reagents is that of hydrofluoric acid, for this reacts vigorously with silicates. The action results in the formation of gaseous silicon fluoride, and, in time, the complete disruption of the glass. The action upon sodium silicate is represented by the equation:



More will be said of the action of hydrofluoric acid under the heading of "Etching" (p. 514).

The attack of a moist atmosphere upon glass results in the absorption of appreciable amounts of water, and it is found that glasses best resisting the attack of water condense least moisture upon their surfaces. The condensed water attacks the glass and breaks down the silicates, and a solution of caustic alkali is left on the surface of the glass. When the air contains carbon dioxide, a further reaction occurs between the gas and the alkali, resulting in the formation of a carbonate. In the case of soda glasses sodium carbonate will result—viz.:



* A 2-normal solution of caustic soda contains 80 grams of caustic soda per litre of solution.

† WAY, CAUWOOD, and TURNER, *J. Soc. Glass Tech.*, 1917, 1, 146.

The sodium carbonate so produced when appreciable attack occurs, crystallises out in fine needles upon the surface and the white deposit results in the dimming of the glass. By rubbing off the crystals with a dry cloth the surface of the glass is badly scratched, but the deposit can be removed without damage by washing with water. Washing, however, will not remove the surface layer of silica obtained by the hydrolysis, so that a filmed glass surface can never be satisfactorily cleaned.

Atmospheric attack on potash glasses results in the formation of potassium carbonate, a substance so deliquescent that it does not crystallise out, but leaves a moist, greasy deposit upon the glass when the surface is badly attacked. The attack of moist air on alkali silicate glass is intensified by heating, and Zschimmer,* at 80° C., obtained effects which were visible in twelve hours.

Glasses high in lead oxide or barium oxide content are susceptible to attack by acid vapours in moist atmospheres, and show filming and dulling of the surface. The chief agent in the case of lead glasses has been proved by Peddle† to be sulphuretted hydrogen, and, to a less extent, carbon dioxide, sulphur dioxide, and other acid vapours. With barium glasses the chief cause of filming is acid vapour, such as hydrogen chloride, or sulphur dioxide, the effect of sulphuretted hydrogen being less important.

(59) **Methods of Testing the Durability of Glass.**—During recent years the study of the relative attack of various reagents upon different types of glasses has assumed great importance, particularly in the case of those needed for special purposes where unstable glass would be harmful, such as in chemical and optical ware. In judging the comparative importance of the attack of the different reagents, the conditions under which the glassware is to be used must first be known. The German Reichsanstalt in reporting upon the stability of Jena chemical glass attached primary importance to the action of water, and ignored the attack of alkalis, assuming that all glasses were attacked to much the same extent by the latter reagents. Other investigators, however, have found that by use of alkaline solutions, differentiations in the stability of various makes of chemical ware could be made, and Cauwood, English and Turner,‡ from detailed investigations, have come to the conclusion that chemical glass should be subjected to the action of water, sodium hydroxide, sodium carbonate, and strong hydrochloric acid. The exact conditions governing the method of attack have not, as yet, been standardised, and it is essential in comparison of figures from various sources to know the precise methods which have been employed. The following outline illustrates some of the methods suggested and used.

THE ACTION OF WATER.—Mylius§ ground the glass to powder and subjected it to attack by hot or boiling water for a known period. The method is good for comparing durabilities of glass of varying types, but the amount of surface exposed is much greater than would be the case if the glass were tested whole, as for instance in the form of beaker

* *Zeitsch. Electrochem.*, 1905, **11**, 629.

† *J. Soc. Glass Tech.*, 1921, **5**, 265.

‡ *Ibid.*, 1917, **1**, 188.

§ *Zeitsch. fur Instrumentenkunde*, 1888, **8**, 267.

or flask. Of great importance is the size to which the glass is ground, since the finer the powder, the greater is the surface exposed per unit weight. It is best to take grains of a definite size, lying between two consecutive sieve meshes, say 10 to 20 or 20 to 30 per linear inch. The powdered glass may, with care, be boiled at the bottom of a silica beaker, but it is much more convenient to use a small bag of finely meshed platinum gauze.* In this method it is essential to free the grains from fine dust, a process conveniently effected by a preliminary washing in alcohol.

In place of the powder, glass discs or slabs have sometimes been employed.† In such a case the actual surface area exposed to the attack of the water can be estimated, but only with accuracy when the slab has been ground and polished. The method admits of easier accomplishment than that of the use of powder, since the slab can easily be suspended in a light wire frame in the liquid, but the time necessary for appreciable attack is much longer than in the former case. Thus 5 to 10 grams of powdered glass of size 10 to 20 mesh will give more extensive corrosion in one hour than will a disc of 100 sq. cm. surface area in six hours.

A method largely used for chemical ware is to stand at known temperatures, or to boil, water in contact with a glass surface (of a beaker or flask, preferably the former), of known area for a given period of time. When the vessels tested are of the same size and shape the process gives a good indication of the relative stability of the glasses.

In a critical survey of the above three methods Turner‡ inclines to the two first as likely to give the most consistent results, particularly the use of a powdered sample, since in this case any preferential attack due to cords, striæ, or inequalities of surface is avoided.

In all of these tests the difficulty lies in obtaining a correct measure of the amount of attack occurring. A common method is to find the weight lost by the glass during the attack, a value of somewhat doubtful import, since absorption of water by the glass, with the formation of hydrated products, undoubtedly occurs. Indeed, in some cases the glass has been actually known to gain in weight. It is recognised that the best indication to be the weight of residue obtained when the water is subsequently evaporated to dryness. If it be supplemented by a detailed analysis of the product obtained it is extremely valuable, but, unfortunately, this latter is very tedious and requires a fair amount of manipulative skill.

Very generally, the amount of attack is judged by the amount of alkali left in solution in the water, as determined by titration with standard acid. The alkali may be of two kinds—"free alkali" that is, caustic soda itself, indicated by the titration using phenolphthalein as indicator, and "total alkali," as indicated by the use of methyl orange as indicator. The total alkali includes not only caustic soda but sodium carbonate, sodium silicate, etc., which also may be obtained by the

* *J. Soc. Glass Tech.*, 1922, 6, 102.

† *Ibid.*, 1919, 3, 230.

‡ *Ibid.*, 1922, 6, 30.

aqueous attack. It will be seen from the foregoing equation (p. 52) that the amount of caustic soda liberated will be proportional to the amount of sodium silicate hydrolysed by the water.

Kohlrausch* determined the amount of material dissolved in the water by measuring the increase of electrical conductivity.

Glass surfaces are sometimes subjected to the action of water and steam at high temperatures and pressures, usually in an *autoclave*, a steel vessel, the lid of which can be screwed down so as to render the whole gastight. By placing the glass, with water, in a platinum dish within the autoclave and heating to any desired temperature above 100° C., much larger losses are sustained than when the glass is treated under normal conditions. Although the method enables a classification of glassware to be made, a number of anomalous results have been obtained, and the method is not devoid of suspicion.

A qualitative method of determining the amount of attack by water upon glass—the iodo-eosin test—has been designed by Mylius.† The dyestuff iodo-eosin is soluble in ether, but its alkaline salts are insoluble. The reagent employed is a solution of iodo-eosin in ether which is saturated with water. On dipping the surface to be tested in the reagent for a definite period, *i.e.*, one minute, alkali formed at the surface, through aqueous decomposition of the silicates, unites with the dyestuff and an insoluble pink stain is left on the surface of the glass of an intensity proportional to the amount of attack. The test has been given a quantitative basis by dissolving off the pink stain in a few cubic centimetres of water (the salt, although insoluble in ether, is soluble in water) and matching the colour of the solution obtained against an aqueous solution of the sodium salt of iodo-eosin of known strength.

Mylius distinguishes between two types of iodo-eosin test, the first a test upon newly fractured surfaces, called "*natural weathering*," the second, a test upon surfaces which have first been fractured and then exposed to a moist atmosphere at 18° C. for 7 days, the latter test being named by him, "*climatic weathering*." The two methods, in some cases, give differing results. The "*climatic*" weathering test is largely used for optical glass, with very concordant results.

The weathering test, due to Zschimmer,‡ in which glass is exposed to an atmosphere saturated with water vapour at a precise temperature for different periods, is often employed in the examination of optical glass. One or two days' attack at 80° C. is sufficient to produce pitting and marking of the surface of poor glass, resulting in a distinct dimming of the surface, and microscopic examination in such cases shows granulated areas, crystalline deposits, or clusters of minute drops of liquid. By observation, a qualitative classification of the glasses, according to the intensity of attack, can be made, but the sorting out of glasses by it does not always agree with the results based upon observation of the glasses exposed in instruments at normal temperature over prolonged periods.

* *Ber.*, 1891, **24**, 3560.

† *Loc. cit.*; *Zeitsch. anorg. Chem.*, 1907, **55**, 233, 256; *ibid.*, 1910, **67**, 200: *Silikat. Zeitsch.*, 1913, **1**, 2, 25, 45.

‡ *Loc. cit.*

(60) **The Attack of Alkalis upon Glass.**—The methods used are similar to those employed for water and are principally used for chemical ware. Caustic soda or sodium carbonate of definite strength, generally twice normal (2N), is allowed to stand in contact with the glass at a fixed temperature over a definite period of time. Where the reagent is boiled it must be emphasised that the solution will increase in strength if the water vapourised is allowed to pass away and a reflux condenser must be employed, whilst with boiling solutions of this type superheating and unsteadiness of temperature are likely to occur. A very satisfactory form of apparatus for the boiling test has been designed in the Department of Glass Technology of Sheffield University.* The discs of glass are suspended in a silver wire frame in a silver beaker containing the reagent. On the top of the beaker rests a silver dish containing cold water supplied from a tap and exhausted by a syphon. By this means any evaporation of the liquid in the beaker is prevented. A very suitable plan for attack by alkali is to maintain the temperature of the liquid at 100° C., which is somewhat below the boiling-point, in a thermostat.

The amount of attack cannot be readily measured by the amount of solid matter gained by the solution, nor by the increase of alkalinity, and the only available method is a determination of the loss of weight of the glass.

(61) **The Attack of Hydrochloric Acid upon Glass.**—A solution of hydrochloric acid gas in water, of constant boiling-point (20·2 per cent. acid), is the reagent used by Turner. Weber† "*weathered*" the glass by first exposing it to the action of hydrogen chloride vapour and afterwards to air.

TABLE XXI.—THE ACTION OF REAGENTS UPON GOOD AND POOR GLASSES.

	<i>Loss in Weight in Milligrams per Square Decimetre.</i>	
	A	B
WATER TESTS:		
(1) 300 c.c. of distilled water boiled to 100 c.c. in 2 hours	0·6	6·2
(2) Autoclave tests (183° C. for 3 hours) ..	22·4	1924·4
ALKALI TESTS:		
(3) 2N caustic soda (100° C. for 3 hours) ..	283·8	364·0
(4) N/10 " " (100° C. " ") ..	61·8	111·3
(5) 2N sodium carbonate (100° C. for 3 hours) ..	78·0	364·3
HYDROCHLORIC ACID TESTS:		
(6) 250 c.c. constant boiling acid evaporated to 100 c.c. in 1·5 hours	8·3	5·4

A number of papers have been published which deal with the examination of glass upon lines indicated above. Of chemical glassware tests may be named those of Mylius and Foerster‡ at the Reichsanstalt, of

* *J. Soc. Glass Tech.*, 1919, **3**, 230

† *Polyt. Journ.*, 1863, **171**, 129; *Ann. Phys. Chem.*, 1879, **6**, 431.

‡ *Zeitsch. anal. Chem.*, 1894, **33**, 381.

Walker,* and of Nicolardot.† The detailed comparison of a large number of "chemical" glasses has been carried out by Cauwood, English, and Turner (a reference to which has already been made), who showed the futility of attempting a clear comparison of glasses from a few tests in cases where the attack was small or the results fairly close together. The foregoing table is illustrative of the type of result they obtained for chemical ware, **A** being a good glass and **B** a relatively poor one.

(62) **Other Tests upon Glass.**—The durability of optical glass may be judged by the amount of alkali extracted from freshly fractured surfaces after a seven days' exposure to an atmosphere saturated with moisture at 18° C., using iodo-eosin as an indicator. According to the amount of alkali extracted, the glasses are placed under headings h_1 , h_2 , h_3 , h_4 , and h_5 , the limits of durability being:

$h_1 = 0-5$	milligrams of alkali extracted per square metre.				
$h_2 = 5-10$	"	"	"	"	"
$h_3 = 10-20$	"	"	"	"	"
$h_4 = 20-40$	"	"	"	"	"
$h_5 = \text{over } 40$	"	"	"	"	"

The results are found to agree extremely well with the stability as found by long usage in optical instruments.

Peddle, by determining the number of milligrams of sulphuric acid needed to neutralise the filtrate after boiling 100 grams of glass (powdered to pass the 160 mesh sieve), for one hour with water, obtained values of durability concordant with those obtained by actual weathering either in moist air for 48 hours or for a week or a year in an ordinary atmosphere.

The correspondence of the two methods is best illustrated by the table given by Peddle† showing his figures for the attack upon Jena glasses:

TABLE XXII.—PEDDLE'S RESULTS FOR THE COMPARATIVE TESTS OF WEATHERING OF GLASS.

Type of Glass.	Schott No.	Order of Weathering from Actual Usage.	Schott Classification.	Milligrams (H_2SO_4 per 100 Grams of Glass).
Light barium flint ..	O 463	1	h_1	159
Borosilicate crown ..	O 144	2	h_2	362
Silicate crown ..	O 337	3	h_3	580
Silicate crown ..	O 203	4	h_4	729
Silicate crown ..	O 381	5	h_5	899

(63) **The Relation between Durability and Composition of Glass.**—The durability of glass is dependent upon the oxides present and also upon the relative amounts in which they occur. We shall treat each of the factors in turn.

* *J. Amer. Chem. Soc.*, 1905, **27**, 865; also WALKER and SMITHER, *J. Ind. Eng. Chem.*, 1917, **9**, 1090.

† *Compt. rend.*, 1916, **163**, 355

‡ *J. Soc. Glass Tech.*, 1920, **4**, 39.

THE RELATIVE EFFECT OF THE OXIDES ON DURABILITY.—It is well known that the presence of large amounts of the alkaline oxides in glass tends to lower its stability and to decrease its power of resistance to weathering. For this reason, pure alkali silicates are quite useless as commercial glasses and other basic oxides must be added, the most common of which are those of calcium, magnesium, lead, and less frequently, barium, in all of which types of glass a decrease of the alkali content makes for durability. The most systematic work on the relative effect of the above oxides in silicate glasses has been given by Peddle* and may be here summarised.

COMPARISON OF SODIUM AND POTASSIUM OXIDES.—In all cases where potash glasses were compared with soda glasses of equal molecular constitution and containing the same second basic oxide (either CaO , PbO , or BaO), the former were more soluble and did not resist weathering so well as the latter. Generally, glasses containing equal numbers of molecules of the two oxides were intermediate in durability between the two single alkali glasses. Where glasses containing potassium oxide were compared with those containing the same percentage weight of sodium oxide varying results were obtained. In lime glasses, judged by the amount of alkali dissolved by water, soda-lime glasses were not so good as potash lime glasses. In lead glasses containing less than 20 per cent. of alkali, potash glasses had an increased stability, but the weathering of the two kinds by exposure was pretty much the same with an alkali content below 15 per cent. It is remarkable that in almost all cases examined, the glasses containing equal percentage weights of sodium and potassium oxides together were much better in regard to their durability than glasses containing the same weight of alkali but in the form of one oxide only. The most stable of all types was the one containing 7 parts of K_2O to 3 parts of Na_2O by weight.

CALCIUM OXIDE AND LEAD OXIDE.—Compared molecularly, lead glasses were less soluble and weathered better than lime glasses providing that the alkali content was less than 15 per cent. Weight for weight of the oxides, lime glasses were more durable than lead glasses. In both cases, when the alkali was kept constant, a replacement of silica by the basic oxide resulted in the increased durability of the glass.

LEAD OXIDE AND BARIUM OXIDE.—Lead glasses were found in all cases to be less soluble in water than barium glasses, but the two were very similar in regard to the effect of atmospheric weathering.

OTHER OXIDES.—*Aluminium oxide*, by a large amount of general evidence, has been shown to be a valuable constituent, helping to give stability towards water, acids, and alkalis. A comparison of soda-magnesia silica glasses with corresponding soda-lime silica glasses indicates that there is little to choose between the two types as regards durability, so that *magnesium oxide* is similar in its effect to calcium oxide in this respect. *Zinc oxide* is used in a large number of resistant glasses, and its value has been indicated by Peddle.† Turning to acidic oxides, *silica* is well known to confer good durability when present in considerable amounts. It can be replaced with advantage, however, to some degree by several of the basic oxides, and by *boric oxide*, and the silica

* *J. Soc. Glass Tech.*, 1920 and 1921, 4 and 5. † *Trans. Opt. Soc.*, 1921-22, 23, 122.

content of most chemical glasses is somewhat lower than that of the most durable soda-lime glasses. *Boric oxide* is extremely useful in increasing the resistance of glass towards water, but only when added to a certain concentration (about 12 molecules to 100 molecules of silica), above which point its effect declines.* Towards hydrochloric acid † and alkali the durability of glass is weakened by boric oxide.

The compositions of a few typical chemical glasses are given in Table XXIII.

TABLE XXIII.—THE COMPOSITION OF CERTAIN CHEMICAL GLASSES.

Glass	PERCENTAGE AMOUNTS OF OXIDES.										
	SiO ₂ .	Al ₂ O ₃ .	ZnO.	CaO.	MgO.	K ₂ O.	Na ₂ O.	B ₂ O ₃ .	MnO.	Fe ₂ O ₃ .	As ₂ O ₃ .
Jena ..	64.58	6.28	11.78	0.08	0.12	Trace	7.38	10.03	Trace	0.10	Nil
E (English) ..	66.38	6.60	8.66	0.49	0.12	1.09	10.02	6.92	Trace	0.10	Nil
Pyrex ..	80.62	2.00	Nil	0.22	0.29	0.61	3.83	11.90	Trace	0.12	0.66
Fry ..	66.58	2.90	3.60	2.65	2.53	1.29	10.01	8.0	Trace	0.26	0.18
Kavalier ..	75.90	0.24	Nil	8.73	0.15	7.84	7.29	Nil	Trace	0.10	Trace

(64) **The Effect of the Molecular Composition of Glass upon Durability.**—Turning now to the soda-lime and potash lead-oxide glasses which comprise the great bulk of ordinary ware, it has for some time been known that there is a definite ratio in which the oxides should be present in order to give maximum durability to the glass. Benrath stated that the most stable form has a composition lying between the limits $\text{Na}_2\text{Si}_3\text{O}_7 + \text{CaSi}_3\text{O}_7$ and $5\text{Na}_2\text{Si}_3\text{O}_7 + 7\text{CaSi}_3\text{O}_7$, whilst in the formula potash could be substituted for soda and lead oxide for lime. Restating the formula in the form of relative numbers of oxides present, the limits become $1\text{R}'_2\text{O}$, $1\text{R}''_2\text{O}$, 0.6SiO_2 and $\frac{2}{3}\text{R}'_2\text{O}$, $\frac{7}{6}\text{R}''_2\text{O}$, 0.6SiO_2 ($\text{R}'_2\text{O}$ denoting "alkali" oxides, and $\text{R}''_2\text{O}$ dibasic oxides). This formula is based upon a ratio of one molecule of base to three of acid, known as a "trisilicate" ratio.

Weber, ‡ whilst agreeing with the trisilicate formula, suggested that where the ratio of $\text{R}'_2\text{O}$ base to $\text{R}''_2\text{O}$ base is less than one, the number of acid molecules should exceed three, whilst with a ratio of $\text{R}'_2\text{O}$ molecules to $\text{R}''_2\text{O}$ molecules greater than one, the number of acid molecules should be less than three.

A more complete statement of the ratio was given by Tscheuschner, § according to whom, when the composition is expressed by $x\text{R}'_2\text{O}$, $y\text{R}''_2\text{O}$, $z\text{SiO}_2$, the acidity for really stable glasses is expressed by the equation

$z = 3\left\{\frac{x^2}{y} + y\right\}$. Taking y , the number of molecules of the dibasic oxide (i.e., lime, etc.), as unity, the formula becomes $z = 3\{x^2 + 1\}$.

Koerner || has given a modification of the Tscheuschner formula, since

* TURNER, *J. Amer. Cer. Soc.*, 1924, 7, 313.

† Hodkin and Turner found that a little boric oxide in lead glasses increased the resistance of these towards hydrochloric acid. See "*J. Soc. Glass Tech.*," 1920, 4, 123.

‡ *Polyt. Journ.*, 232, 349.

§ *Handbuch der Glasfabrikation*, Leipzig, 1885.

|| *Sprechsaal*, 1915, 48, 332

he contends that potash-lime glasses require more silica to render them resistant. According to him, if all the alkali be potash, the formula expressing the molecular relations necessary for a good glass becomes more nearly $z = 4\{x^2 + 1\}$. If both soda and potash be used, the expression must be modified as follows: (a) sodium oxide preponderating, $z = \left(3 + \frac{x_K}{x}\right)\{x^2 + 1\}$, and (b) potassium oxide in excess, $z = \left(4 - \frac{x_{Na}}{x}\right)\{x^2 + 1\}$, x_K and x_{Na} being the number of molecules of potassium oxide and sodium oxide respectively. In its simplest form the trisilicate ratio has proved extremely effective in guiding the manufacturer in the problem of the compositions of glass and of batch. The batch corresponding to the molecular ratio $1Na_2O, 1CaO, 6SiO_2$, is given below:

Sand, 1,000	..	{ Quicklime, 155 Slaked lime, 204 Limestone, 276 }	}	Soda ash, 293. Saltcake, 392.

The composition of the glass obtained from this batch will be SiO_2 75.4 per cent., CaO 11.7 per cent., Na_2O 12.9 per cent. In practice, durability is not the only factor to be considered, working properties influencing the choice of the batch. For this reason, although the trisilicate ratio is generally favoured, it is usually modified to about $0.8Na_2O, 1.2CaO, 6SiO_2$ for hand-made bottles and window glass, and $1.2Na_2O, 0.8CaO, 6SiO_2$ for machine-made bottles, although more extreme variations than these are frequently met.

A potash-lead-oxide batch for the stable glass $1K_2O, 1PbO, 6SiO_2$ would be, sand 1,000, red lead 616 to 630 (according to its composition) potassium carbonate 380, giving a glass of the composition 53.3 per cent. SiO_2 , 32.8 per cent. PbO , 13.8 per cent. K_2O , figures closely approximating to those of the usual type of "English crystal" glass.

For more complex glasses, chemical ware for instance, the trisilicate ratio is found to hold approximately for most of the best commercial products. In the series examined by Cauwood, English, and Turner the following ratios of acid to one molecule of base were found in the case of the best glasses: 3.7, 2.3, 3.2, 2.85, 3.4, 3.1, 3.2 (the position of alumina is at present in doubt, as it may have acidic functions, but it is included in the basic oxides in the above calculations).

That the above generalisations cannot be applied to all glasses is evidenced by the case of Pyrex glass, a good resistant glass with a ratio of base to acid of 1 : 15.3. Peddle recommends, as a ratio for a good all round soda-lime glass, the formula $5SiO_2, 1R'_2O, 1CaO$, and for the best lead glass the ratio $5SiO_2, 1R'_2O, 1.5PbO$.

CHAPTER VII

THE RAW MATERIALS USED IN GLASS MANUFACTURE

(65) **The Classification of Glass-making Materials.**—As a general means of classification of glass-making materials, two methods are open to us—the first, a technical one based on the specific uses of the various substances; the second, a division based upon their chemical properties. In actual practice it is found convenient to combine the two methods. From the technical point of view materials fall into the groups—(a) essential glass-forming substances, (b) fluxes, (c) oxidising agents, (d) fining agents, (e) reducing agents, (f) colouring agents.

We have seen in our study of the composition of glass, that the salts of which it is composed may be considered as compounds of acidic oxides with basic oxides, and so we may subdivide our essential glass-forming materials into those which produce acidic oxides and those which produce basic oxides in the glass. It is not possible in every case to use the oxide itself, and often, even when it is possible, it is not always desirable, such questions as cost and suitability for handling, storing and mixing influencing the choice of the material used. In such cases, other oxides or salts, capable of reacting suitably during the fusion, are employed. Some of the fining and colouring agents contribute to the quota of basic oxides present, but, generally, only to a very small extent.

We now come to the consideration of the essential glass-forming oxides, of which the first subdivision is acidic oxides. The most important of these is *silica*.

(A) Acidic Oxides.

(66) **Silica** (*Formula*, SiO_2 . *Molecular weight*, 60).—Silica, which is found as an important constituent of every commercial glass, is widely distributed in Nature, both in the free state and in the form of its compounds, the silicates. The varieties of natural silica may be classed under the following heads: (1) Crystalline silica, *quartz*, *tridymite*, and *cristobalite*; (2) cryptocrystalline silica (the crystals being obscure or extremely minute), *flint*, *chert*, *chalcedony*, *agate*, *jasper*; (3) *amorphous silica*, such as *opal*.

Quartz occurs in the form of crystals having the shape of hexagonal prisms terminated by hexagonal pyramids (see Fig. 14), although completely formed crystals are not common. Tridymite, although of the same chemical composition as quartz, has a different crystalline form, occurring in small, triple, hexagonal plates. It is formed when quartz is heated for a long time at high temperatures. Cristobalite, the third

crystalline form of silica, occurs in small octohedral crystals. Of these forms, quartz is by far the most common, forming, according to F. W. Clarke, about 12 per cent. of the earth's lithosphere. In its purest form it is known as *rock crystal*, whilst *amethyst*, *rose quartz*, *cairnngorm*, and *aventurine* are forms of the less pure material coloured by various oxides. But the great bulk of the quartz occurring in Nature is found as a constituent of the great masses of the igneous rocks and of their decomposition



FIG. 14.—A QUARTZ CRYSTAL.

products, sands and sandstones. Igneous rock are those which have crystallised out from a liquid magma, such, for instance, as a volcanic lava. The compounds which have crystallised out from this liquid mass are silicates such as *felspars*, *micas*, *hornblende*, *augite*, etc., and in some cases, where the silica content of the matrix has been high, of quartz itself. The acid igneous rocks in which quartz is found are *granite*, *quartz porphyry*, *rhyolite*, and *obsidian*, the total silica content of these being of the order of 65 to 75 per cent. In the case of granite the cooling and resulting crystallisation has been very slow and consequently the crystals are large and the structure coarse, rock of this kind being called *plutonic*. On the other hand, *rhyolite* and *obsidian* have been formed from a rapidly chilled magma, one which has penetrated on to or near to the surface of the earth before cooling; hence its crystals are minute, and the structure fine, and difficult or impossible to distinguish. In these acid rocks, quartz has generally been the last mineral to crystallise, and has moulded itself upon the crystals which have previously formed, filling up the interstices of the rock, although occasionally quartz and felspar have crystallised simultaneously.

(67) **The Weathering of Rocks.**—Nature is a constant worker, and wherever igneous rocks have been left exposed, they have been subjected to persistent wear and tear. Water has penetrated into them and, freezing, has torn fragments away. Changes of temperature with the expansion and contraction of the rock, due to heating and cooling, have added their quota to the destruction, whilst wind and rain have battered at the crumbling rock and helped to break it down. This explains the presence, in granite districts, of large blocks of rock strewn the hillsides, and of pebbles in the valleys of the streams below. Though mechanical action is important, it is not the only way in which rocks are subjected to destruction, the chemical action of rain water being a vital factor. Pure water can dissolve many substances composing the earth's crust, but, alone, would have no action upon the materials composing igneous rocks. Rain water, however, is not pure, but contains in solution the gas carbon dioxide, such a solution being acid in character; hence its name—*carbonic acid*. Though a weak acid, carbonic acid is capable of cor-

Having now discussed the methods of formation of the principal silica-bearing materials of nature, it remains to decide which of these are the most suitable for the production of silica in sufficient quantity and purity for use in the manufacture of glass. It is evident that igneous rocks are out of the question for this purpose, since the amount of free silica in them is relatively small, and it would be impossible to separate it from the other constituents of the rocks. The remaining deposits, sands, sandstones, and quartzite rocks, are all possible sources of silica, and circumstances must dictate which of these are the best to employ. It may be said, however, that, other things being equal (that is, accessibility, quantity available, cost of transport, etc.), sands will be the most suitable, since rocks must first be reduced to the necessary fineness of division, a process involving expense, both in plant and labour. In some cases, particularly, as we shall see later, in the United States of America, the occurrence of siliceous rocks, suitable for crushing, of great purity and in large quantities, renders the use of this material commercially possible, especially since there are few sand deposits of equal purity available. We may say, however, that the general source of silica for glass-making is sand.

(68) **Sand.**—The term “sand” is given, geologically, not to a substance of definite composition, but to one consisting of grains of a definite size. Sand is thus a mineral with a large percentage of grains of diameter lying between 1·0 and 0·1 millimetre. Sands which are very coarse may have a grain size of diameter ranging as high as 2 millimetres, whilst we may find “superfine” sands with grains of a diameter as low as 0·05 millimetre. Above 2 millimetres diameter the grains form gravel, whilst below 0·05 millimetre we get silts, clays, and mud. The usual division of sands according to grain size is as follows:

Above 2 millimetres diameter	..	Gravel.
From 2 to 1 millimetre diameter		Very coarse sand.
From 1·0 to 0·5 millimetre diameter		Coarse sand.
From 0·5 to 0·25	“	Medium sand.
From 0·25 to 0·1	“	Fine sand.
From 0·1 to 0·05	“	Superfine sand.
From 0·05 to 0·01	“	Silt.
Below 0·01	“	Clay or mud.

We have seen that quartz, being one of the hardest and most stable of minerals, will form, in general, a large portion of the sands which are transported and laid by the action of water. This, though the rule, has its exceptions, as, for instance, in the case of monazite sands, which consist largely of calcium and lanthanum phosphates and contain up to 10 per cent. of thoria. Such sands are rare in extent and occurrence as compared with the highly quartzose sands found in abundance in all parts of the world. Those sands which have longest been subjected to the action of water will be the richest in quartz, especially, as we have previously seen, in cases where the material has been repeatedly formed into rocks and again broken up by weathering. They will also be the most evenly graded, though the sorting is never complete, and we generally find gravel, silt, and clay associated with the sand. From the standpoint of the glassmaker, impurities in sand will be all minerals except quartz, for although many of the other minerals usually present are

silicates, these are not suitable for making glass. Such impurities are small pieces of broken rocks, and the minerals derived from them. Heavy detrital minerals, having a density above 2.8, are generally very stable, and so we find few fragments of these in the sand, the amount seldom reaching 5 per cent. Amongst the impurities present are the following: Titanium oxide, (TiO_2), aluminium oxide, (Al_2O_3), the iron oxides—*hematite* (Fe_2O_3), *limonite* ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$), and *magnetite* (Fe_3O_4), calcium carbonate (CaCO_3), and *dolomite* (calcium-magnesium carbonate $\text{CaCO}_3 \cdot \text{MgCO}_3$). Of silicates, we find *felspars* (compounds of aluminium silicate with the silicates of potassium, sodium, and calcium), *micas*, the partial decomposition products of felspars (aluminium silicate combined with silicates of the alkalis, iron, magnesium, and calcium), *hornblende* and *augite* (silicates of aluminium, iron, magnesium, etc.), *enstatite* (magnesium silicate), *garnet* (silicates of magnesium, iron, manganese, calcium, etc.), *zircon* (zirconium silicate), and *clays* (hydrated silicates of aluminium). Many of the above silicates are not definite chemical compounds, but consist of indeterminate mixtures of the component silicates. It is well to point out that the impurities present may occur not only as distinct grains, but in the case of the oxides of iron, clay, calcite, and dolomite, actually as a coating on the surface of the quartz grains, or as a cement holding them together. Where sands have been in contact with organic matter such as decaying vegetable material, purification has often been accomplished, since rain water percolating through the sand then contains humic acid, a product of vegetable decay, and is able to dissolve out impurities, particularly iron compounds. That is why sands laid down in carboniferous times are generally extremely pure.

(69) **The Choice of Sand.**—The chief considerations guiding the manufacturer in his choice of sand are (a) purity, (b) grading, (c) cost. Which of these assumes the greatest importance depends upon the type of glass to be manufactured.

(a) **PURITY.**—In the case of optical glass and of the best crystal ware, extreme purity is required, and the chemical composition of the sand is the first consideration. The desiderata are high silica content, and extremely low iron content. No sand is a first-rate glass sand if it contains less than 99 per cent. of silica, and the silica should be, as far as possible, in the form of grains of quartz. Other impurities than iron compounds, such as the oxides of aluminium, magnesium, calcium, sodium, and potassium, would not, of themselves, be detrimental if in small amount, since they would usually be added to the glass in any case, and none of them give rise to colour. The objection to their presence is that sand containing these oxides in considerable amounts would be liable to variation in composition throughout the bed, a variation which would cause trouble unless properly controlled. In optical glass, again, these impurities affect the homogeneity of the glass and alter the optical constants. For other types of glass, alumina, unless in very high quantity, may not only be harmless but actually beneficial, since, as we have seen, alumina helps to give glass a higher mechanical strength. The same may be said for magnesia, the effect of which on glass has only recently been studied. If the sand contains alumina it usually

denotes the presence of felspar, mica, or clay, and the last named may frequently be reduced in quantity by washing. Calcium oxide in large amounts is generally indicative of the presence of shells which are composed of calcium carbonate. Sand from the sea-shore may contain as much as 30 per cent. of calcium oxide. Such sands might be useful for bottle glass, since calcium carbonate in the form of limespar or chalk is usually one of the constituents of the batch. Indeed, with sand containing the higher amounts of lime, not only would no limestone be needed, but the material would have to be diluted with purer sand to give a batch of suitable composition. The difficulty in regard to these sands is, again, a variability of composition; this, in general, being very great, and precluding their use. The most important impurity in sand is iron oxide, since the presence of a very small amount in the glass produces a noticeable colour, even 0.1 per cent. of iron oxide resulting in a green glass. No high class sand must contain more than 0.05 per cent. of ferric oxide. For the best optical glass a value of iron oxide of 0.02 per cent. or at most of 0.03 per cent. must be considered the limit. For plate glass the limit of ferric oxide present in the sand must be, according to Dralle, 0.2 per cent., or 0.1 per cent. for mirrors. For window and sheet glass an iron oxide content of 0.2 per cent. or 0.3 per cent. would be admissible. The latter type of sand could be used for the better glass bottles. Perfect decolourisation is only obtained with glasses containing 0.09 to 0.1 per cent. of ferric oxide or less, those with higher amount showing a loss of brightness, the depth of colour being dependent upon the amounts of iron oxide and decolouriser present. This means that even if all the other batch materials are pure, a condition extremely unlikely, a sand containing above 0.10 per cent. of ferric oxide will not give good colourless bottles even when "decolourised." In the ordinary course, a limit not in excess of 0.05 per cent. is demanded for good bottle-making sand. For common green bottles, the iron oxide content may exceed 0.5 per cent., whilst for "dark" metal, 3, 4, or even as much as 7 per cent. of ferric oxide may be present. Chemical and similar glassware demand a ferric oxide content not exceeding 0.1 per cent.

(b) GRADING.—This is of the utmost importance in ensuring rapidity and evenness of melting. If the grading is uneven, the fusion proceeds irregularly, and "sandy" or "stony" metal may result. Average fineness of grain is of less importance than freedom from extreme fractions. The sand grade in a first-class sand should not fall far short of 100 per cent., and there are many good sands containing over 95 per cent. of the "fine sand" grade. According to Boswell* the sand should have over 70 per cent., and preferably over 90 per cent., of one grade, the best grade being of medium grain size—i.e., 0.25 to 0.5 mm. diameter. Sands with grains chiefly of the "fine grain" size (0.1 to 0.25 mm. diameter) would be better for melting than those of the larger grades, but sands of this type are not so commonly found pure as sands with larger grains. Consideration of surface area of the grains proves that the smaller the grain the greater its area of surface relatively to its volume, hence the

* *A Memoir on British Resources of Sands and Rocks used in Glass-Making.* London. 1918.

smaller the grain the more rapidly will it react, since the attack of the flux during the formation of glass is a surface action. From this point of view alone, the smaller the grain size the quicker will be the rate of melting, a point of considerable importance. On the other hand, we have seen that smaller grains are not in general so pure, especially where covered with a coating of impurity such as iron oxide, when evidently the ratio of surface coating to the volume of the grain increases with decrease in grain size. For this reason, particles with a diameter of less than 0.1 mm. are a fruitful source of iron impurity. As an example, Peddle,* on sieving a sample of Huttons Ambo sand and examining the iron oxide content of each fraction, obtained the following figures:

Grain Size in Millimetres.	Percentage of Fe_2O_3 .
0.5 to 0.3	0.29
0.3 „ 0.22	0.22
0.22 „ 0.16	0.31
0.16 „ 0.12	0.80
Below 0.12	1.25

Kümmel and Gage† came to the same conclusions on sieving a sand through an 80-mesh sieve and analysing both the original sand and the larger-grained fraction after sieving. Their figures were:

Percentage of—	Before Sieving.	After Sieving
Fe_2O_3	0.068	0.022
TiO_2	0.117	0.024
Al_2O_3	0.276	0.085

A further trouble in the case of small grains is that they cause the formation of fine seed, difficult to remove. Again, when used in a tank furnace, there is a tendency for them to be carried away by the draught into regenerators and flues.

The shape of grain is also of importance, since the more angular the grain the greater is its surface area, and consequently the more rapidly it will melt. This factor, though important, is not vital, and American glass sands, in general, possess beautifully rounded grains.

Other factors of great importance in choosing any particular sand are that consignment after consignment should be true to sample, and that the sand should be placed on the market with regularity and in quantity. That these factors carry great weight is seen when we consider the number of English sands which occur, or are quarried, only in small amount or varying composition. Speaking of Godstone sand, for instance, Boswell‡ states that “*the sand has been sold for glass-making, but never in quantities of more than 90 tons per week, a hopelessly small amount.*”

(c) COST.—Other factors having been considered, the cost of varying sands will be a prime factor in the choice of a sand. Since, in general, the manufacture of glass is carried on in, or near, coal producing areas, factories are not always located in the best positions for the cheap supply of good sands. The problem is rendered more difficult in England by

* J. Soc. Glass Tech., 1917, 1, 27.

† Geological Survey of New Jersey, Annual Report, 1906, pp. 77 to 96.

‡ Loc. cit.

the comparatively poor facility for its carriage, with consequent high transport charges. In America, special railway trucks allow of the easy movement of large consignments of sand over considerable distances, giving the manufacturer greater freedom of choice. Distant sands should not be used in general, until the unsuitability of local sands has been proved by examination and analysis

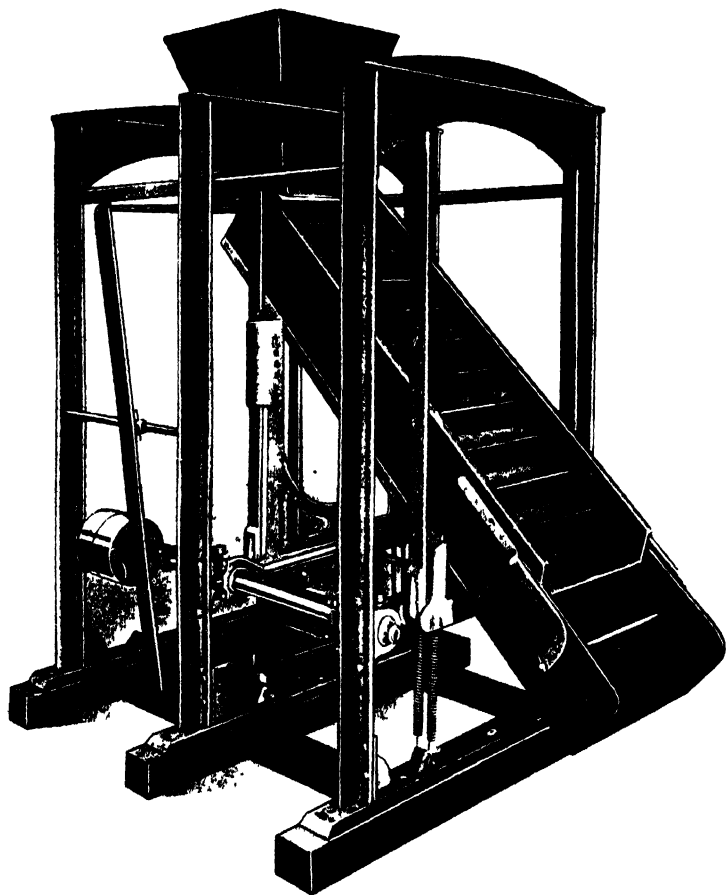


FIG. 15.—AN ELLICOTT-MAGNETIC SEPARATOR.

(By courtesy of The Rapid Magnetizing Machine Company, Ltd., Birmingham).

(70) **Crushed Rocks.**—Where good sands are not available the remaining sources of silica are sandstones and quartzites. Should these occur in sufficient purity for use, they must be crushed to the requisite fineness. The silica grains in some quartzites and sandstones are so firmly bonded together that crushing is difficult, the rupture even occurring in some cases across the grains rather than along the bonds. Rocks of this type

would cost too much to crush, and the resultant powder would be too uneven in grading for general use. It has been suggested that a preliminary heating would give an initial breaking up of the large rock fragments, and so facilitate crushing, but the authors know of no places where this treatment is yet used. The great objections to the crushing of rocks are the cost of the process, the unevenness of the grain of the resultant sand, and the tendency to iron contamination caused by disintegration of the grinding apparatus. The first difficulty is inherent in the method, and though, by treatment of large quantities of rock, it may be reduced in proportion, it always results in a higher price necessary for the resulting sand. Uneven grain size is also characteristic of sands obtained by crushing rocks, and although it is counteracted by the screening and washing of the products, it nevertheless results in a large wastage of material. Even after treatment, the sand is not so even as that graded by nature. The third fault, that of iron contamination, is, in the case of some American sands, minimised by extracting the metallic particles by means of an electro-magnetic separator.

A separator of this type, made by The Rapid Magnetizing Machine Co., Ltd., of Birmingham, is illustrated in Fig. 15. Generally speaking, the material is fed into the hopper, under which is fixed a "shaker" feed tray, which automatically discharges the material. The separator shoot being inclined (adjustable) and oscillating laterally at 250 movements per minute, the material is caused to travel down over the bars, which are electro-magnets. Any iron particles lying on the surface of the material sink by gravity until they must inevitably come into contact with the magnets, and be there held. It follows, naturally, that having a series of magnets to pass, if the first fails to secure the iron particles, each of the others in turn has a chance.

(71) **The Treatment of Rocks and Sands.**—Rocks, after crushing, are treated much in the same way as sands, and so the process of crushing the rocks will be considered first.

THE CRUSHING OF ROCKS.—The following, an account of the methods used in West Virginia near Berkeley Springs, is representative of the general process in use. Usually, shallow holes are drilled with tripod or hand hammer, compressed-air drills, and the rock is then blasted. By this means irregular blocks and much fine material are obtained. The quarry face is usually of a depth of 50 to 100 feet, and is almost perpendicular, and the rock tends to form more or less rounded pieces which roll to considerable distances. The detached blocks can generally be broken to loading size with sledge hammers, and, coarse and fine together, the material is loaded on to small narrow-gauge railway cars and hauled by horses or mules to the crushing plant. For crushing, small jaw crushers of the Blake type (see Fig. 16) of a size 12 by 20 inches are usually used, the rock being reduced to lumps about 3 inches in diameter. The crushers are fed from wood bins with hopper bottoms, holding from 25 to 200 tons. On leaving the jaw crushers water is mixed with the material, and the whole flows by gravity to chaser mills or pug mills. A mill of this type, made by the Lewistown Foundry and Machine Company, consists of a pair of cast-iron or steel wheels revolving rapidly on a horizontal shaft, pivoted at its centre

and revolving on a vertical shaft. Grinding is performed at the bottom of a watertight pan, where the grinding wheels are in contact with a hardened steel ring. The pans and cylinders enclosing the mill are about 9 feet in diameter. Screens at the side of the pan, of 10-mesh, allow the material to wash through when sufficiently ground, the water being sufficient in amount to carry the fine sand in suspension. The sand and water from the mill flow by gravity to two horizontal cylindrical screens, 6 feet in diameter and 30 inches long, of 12-mesh, made of brass wire. Material failing to pass the screens is returned to the mill. Washing of the ground sand is done by screw washers, and will be described later.

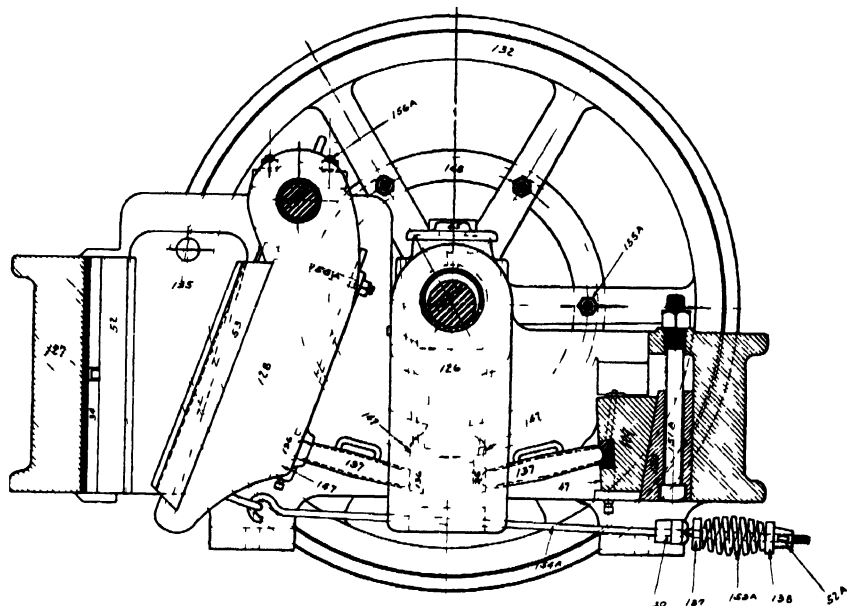


FIG 16.—THE LEWISTOWN STANDARD BLAKE TYPE CRUSHER

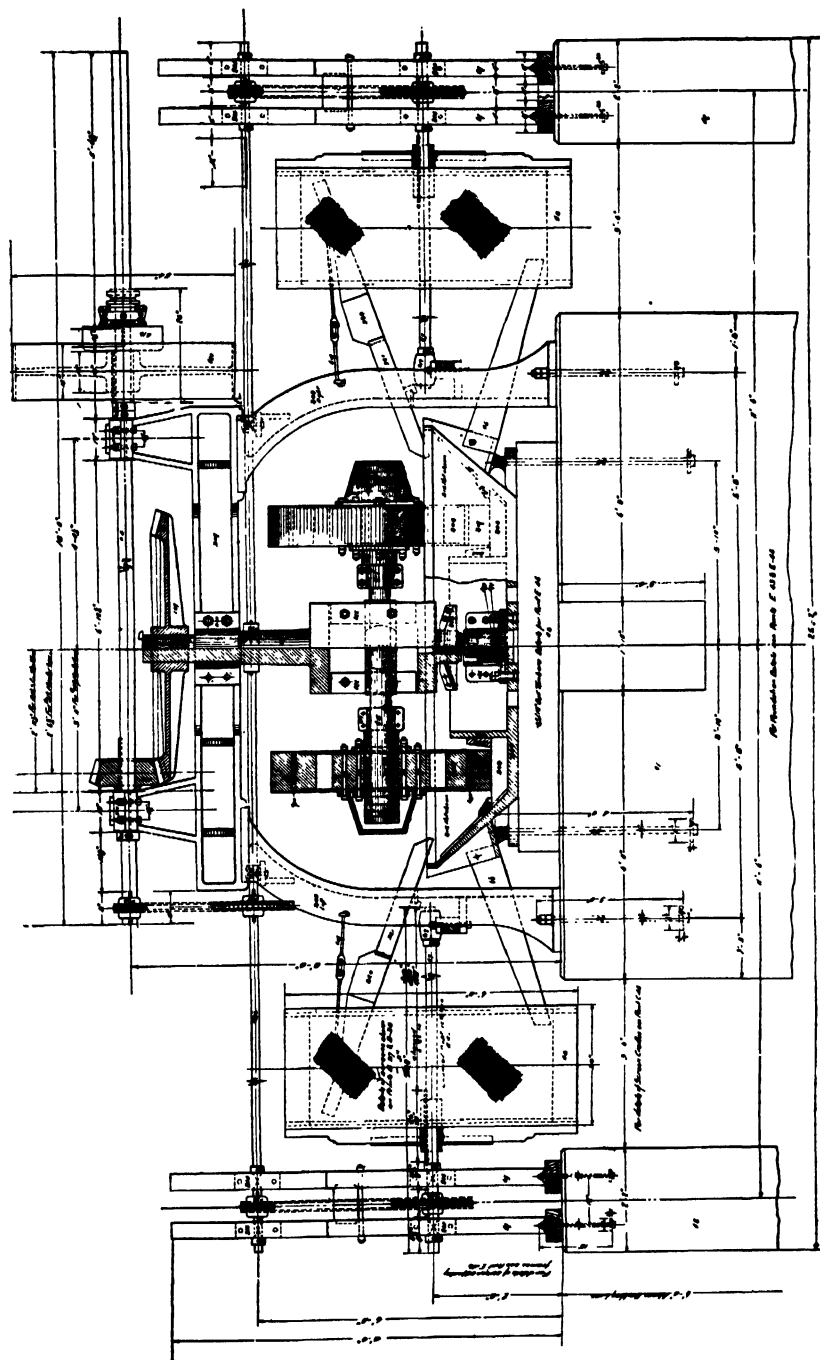
(By courtesy of the Lewistown Foundry and Machine Company, Lewistown, Pennsylvania.)

Some of the American sands are ground in the dry state, without subsequent washing, and in this case a different type of grinding mill is employed.

The mill rollers revolve on a stationary horizontal axis, and the pan also rotates. The outer portion of the bottom of the grinding pan is in the form of screen plates, and, when ground, the sand falls through on to revolving or shaking screens, where it is finally sieved.

(72) **The Purification of Sands.**—As there are very few sands sufficiently pure in the natural state for making good quality glassware, it is well to enquire if it is possible to improve the quality of the many sands falling somewhat short of the requisite standard of purity.

Improvements in glass-making sands may be made both by chemical and mechanical methods, but whereas the former are costly and scarcely



Lewistown Foundry and Machine Co., Lewistown, Pa.

STANDARD 9-FOOT CHASER MILL AND SCREEN
FIG. 16A.

admit of extensive practical application, the latter are comparatively cheap and may be used on a commercial scale. As examples of successful chemical treatment on a small scale, Boswell* states that sand from Eaglescliffe, treated with nitre-cake (the residual acid sulphate cake from the manufacture of nitric acid), was reduced in ferric oxide content from 0.20 per cent. to 0.05 per cent. Treatment of Leighton Buzzard sand with sodium carbonate reduced the ferric oxide from 0.04 per cent. to 0.015 per cent.

Peddle,† on the other hand, states that Huttons Ambo sand treated for 14 days with cold hydrochloric acid showed no improvement in regard to the colour of the glass that it produced, and the same was true if the sand was digested for 6 hours with the hot acid.

Ignition of the sand removes water and organic matter, such as peaty residues or coal-dust adventitiously introduced during transit. This method of cleansing is suitable for high-class ware, particularly for sand used in producing lead crystal glass.

The chief modes of purification remain, however, the mechanical methods of washing and sieving. In the formation of sands the grading action of the water is never complete, and a more thorough washing, such as is obtained by driving the sand against a stream of running water, is effective in removing the finer material, consisting chiefly of clay and extremely fine grain sand. But it does more than this, for we have seen that the fine matter is richer in iron content, and so washing improves the quality of the sand also. Sieving serves to remove the largest and the smallest grains, giving a product with a more even grain size, and also to purify the sand. When the two methods are combined the effect on the purity of the sand is well marked. As an example, Peddle,‡ on treating a sample of Fontainebleau sand, found the following changes to occur:

				<i>Before Washing and Sieving</i>	<i>After Washing and Sieving</i>
				<i>(Percentage Composition).</i>	
Silica	99.60	99.78
Alumina	0.21	0.16
Ferric oxide	0.03	0.025
Loss on ignition	0.12	0.03

It is obvious from these figures that even a high class sand is improved by washing and sieving.

(73) **Methods of Sieving and Washing.**—The method of treatment of American sandstones after sieving (the screening has already been described) is to drive the sand through inclined wooden troughs against a current of descending water, the sand being raised in the trough by means of iron conveyer screws. The troughs are 10 to 12 feet long and 18 to 22 inches wide, and they are set up in batteries. Fig. 17 illustrates screw or log washers as made by the Lewistown Foundry and Machine Co. A battery of washers consists of four parallel troughs or logs through which the sand passes in series, up one and back by the adjoining one. The lower ends of the washers are provided with settling tanks from

* *J. Soc. Glass Tech.*, 1917, 1, 21.

† *Ibid.*, 1917, 1, 50.

‡ *Ibid.*, 1917, 1, 27.

which the dirty water overflows into waste chutes. A fresh supply of water is provided for each trough, and the sand has thus four washings of fresh water. Sand is discharged from the washers at the upper end of the trough. It may be stated here that a 9 foot chaser-mill with two cylindrical screens (6 feet by 2 feet 6 inches) is usually provided with two batteries of washers of four logs each, and the unit is capable of grinding and washing about 200 tons of sand per day.

A convenient type of washing and screening machine for sands in use in England is that of Rikof. It consists of a long, slightly inclined, rotating cylinder, into which sand is uniformly delivered by a special feeding device. The length of the cylinder is adjusted to suit the type of sand under treatment. It is divided into compartments, the sand being automatically propelled from section to section down the cylinder, over the dividing partitions against a current of water. On emerging from the tube the sand passes through a series of screens, in the form of

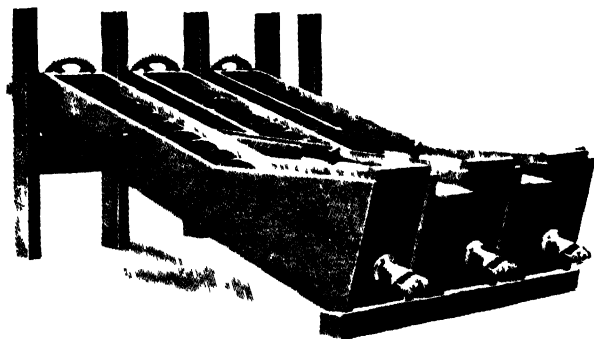


FIG. 17.—SAND WASHERS (SCREW TYPE)

(By courtesy of the Lewistown Foundry and Machine Company, Lewistown, Pennsylvania)

concentric cylinders, of which the innermost has the largest holes, and into this the sand is fed. As the sand passes successively through the screens, towards the outermost, the holes decrease in size and grading is obtained, screening being helped by sprays of water which also give a final washing. The machine possesses a special sediment separator whereby the stream from the screens is caught in pockets on a rotating cone, the sand is allowed to rapidly settle, and is tipped into a heap, whilst the water drains away. The Hardy and Padmore sand washer, as illustrated in Fig. 19, is of the paddle type. Sand to be washed is thrown into the revolving screen **H**, where it is sprayed with water and finds its way into the trough pipe **A**, larger grains, stones, etc., passing into the chute **K**. Along trough **A**, through which the sand is now driven, are a series of hand-shaped stirrers on the shaft **E** and a series of conveyer blades; washing is performed by a water current passing in an opposite direction to the sand. On leaving trough **A** the sand falls through box **D**

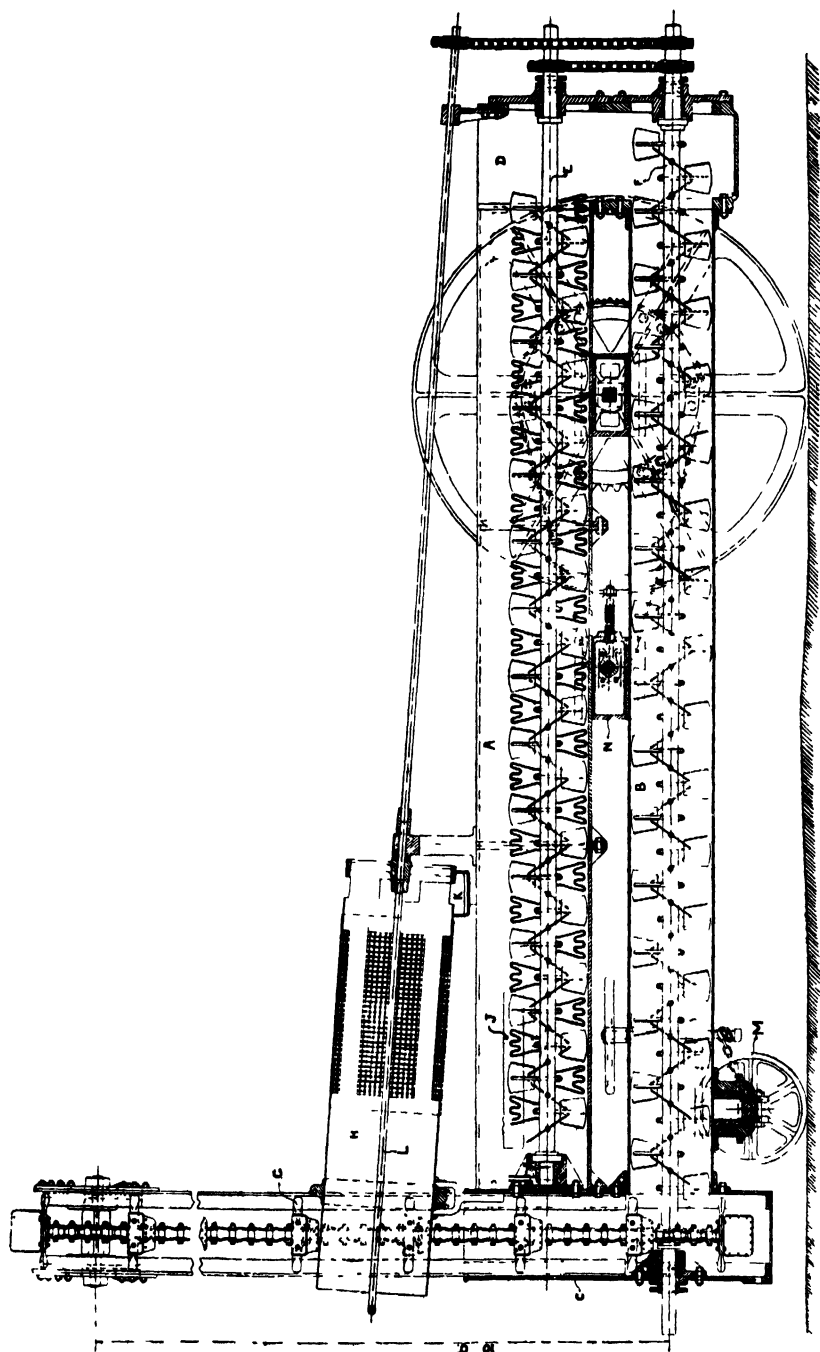


FIG 18—A SAND WASHER (PADDLE-TYPE).
(By courtesy of Messrs. Hardy and Padmore, Ltd., Worcester.)

and is driven along trough **B** into tank **C**, is then lifted by elevator buckets and dropped clear of the machine.

The Koerting washer consists of a series of iron boxes, and sand is forced from one to another of these through tubes by jets of pressure water (see Fig. 19). As the sand passes into each box it falls to the bottom and is stirred by a jet of water, which carries away the clayey material and overflows near the top of the box.

(74) **The Drying of Sands.**—After the washing of the sand the question of drying occurs, since, from the glass manufacturers' point of view, a fairly dry sand is to be preferred. A perfectly dry sand, however, causes difficulty in transit, and so the sand is generally delivered as "drained" or "air-dried."

One American method of draining is to run the sand from the washers along conveyer belts passing close to the roof of the drying shed. The sand is dropped at a number of points, and forms cones on the drying floor, where it is allowed to drain for 12 hours or more. Where the sand is so dried in heaps, a system of open-joint tile drains under the floor

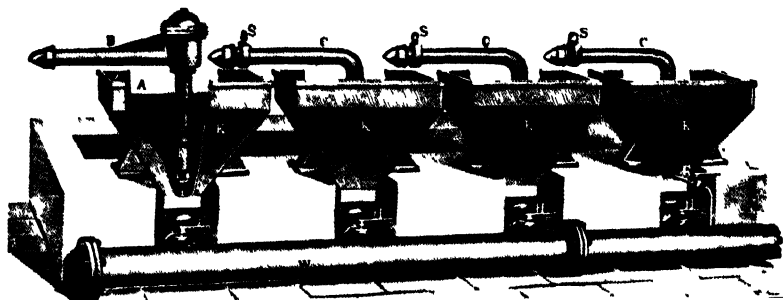


FIG. 19.—A SAND WASHER (KOERTING TYPE).

allows the water to drain away. Usually, the drained sand is at once conveyed to dryers by means of overhead cranes with grab-buckets or conveyer belts.

Drying is carried out by two methods, direct heating by means of hot gases, and steam drying. Fig. 20 illustrates a simple type of dryer made by Hardy and Padmore, in which the sand is dried by heat developed from gas ring burners situated under a series of pans placed in a vertical tier. Damp sand is carried on to the top pan by elevator buckets, and is driven round the pan by arms attached to a central revolving spindle, until it drops through a hole in the bottom of the pan on to the second pan, the process being repeated until the sand reaches the bottom. Another type of dryer by the same firm (Figs. 21 and 22) consists of a horizontal rotating cylinder through which the sand is driven by the rotation. Heating is performed by coal or gas whilst a fan draws air through the apparatus. The Cummer dryer (made by F. D. Cummer and Son, Co. Cleveland, Ohio, U.S.A.) consists of a cylinder revolving in a chamber into which hot gases pass (see Fig. 23). The wet sand is

fed regularly into one end of the dryer through a feed spout and delivered continuously at the other. In the revolving cylinder are a number of 8 by 8 inch holes spirally arranged so as not to weaken the cylinder, each hole being covered by a hood to allow of free entry of the gas without the possibility of choking by the sand. About three-quarters of the

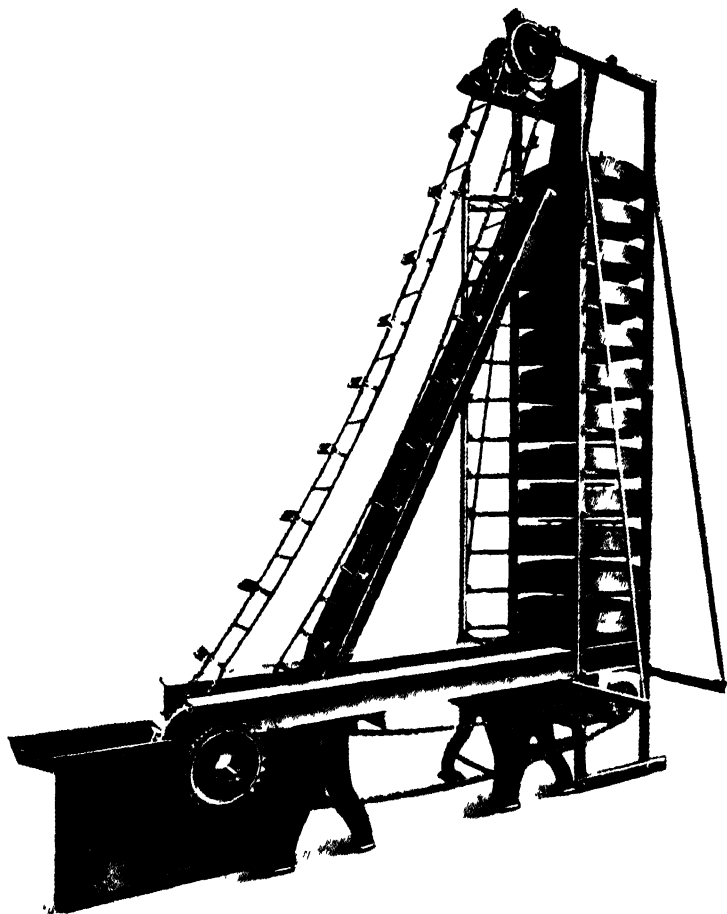


FIG. 20 —A SAND DRYER.

(By courtesy of Messrs. Hardy and Padmore, Ltd., Worcester.)

heated air and products of combustion enter the cylinder through the hoods, whilst the remainder passes in at the rear end of the tube. A fan, fixed at the front end of the apparatus, draws gases regularly from the furnace into the heating chamber around the cylinder, and through the cylinder itself. The cylinder is slightly inclined and has lifting angles to cascade the sand and gradually carry it to the discharge end.

In the case of dryers heated by furnace gases the hot sand must not be allowed to come into contact with woodwork or inflammable material.

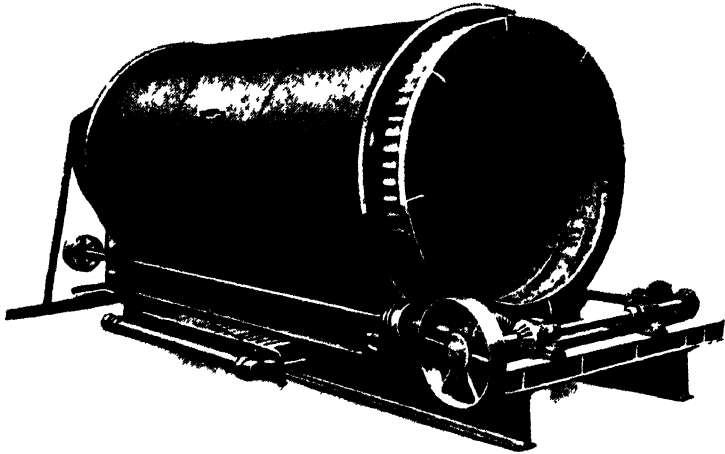


FIG. 21 —A SAND DRYER (VIEW FROM CHARGING END).
(By courtesy of Messrs. Hardy and Padmore Ltd., Worcester)

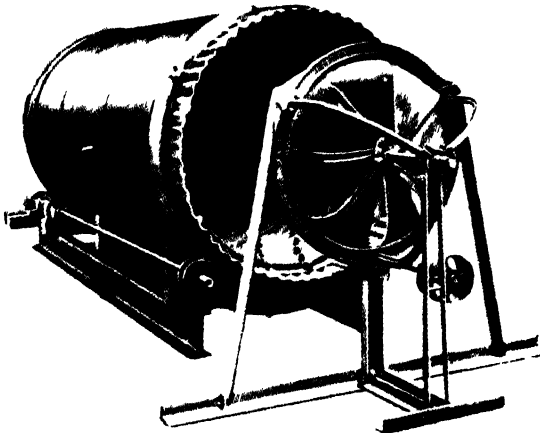


FIG. 22 --A SAND DRYER (VIEW FROM DELIVERY END).
(By courtesy of Messrs. Hardy and Padmore, Ltd., Worcester)

A crude type of steam dryer sometimes used consists of an iron plate with steam pipes below, sand being spread and turned over on the plate until it is dry. A Spear steam dryer, made by the Lewistown Foundry and Machine Co., consists of tiers of steam pipes in a long horizontal

box with hopper-shaped bottom (see Fig. 24). The openings between the pipes decrease towards the bottom of the dryer. Sand is fed through a hopper on the top of the dryer, passes down between the pipes, and

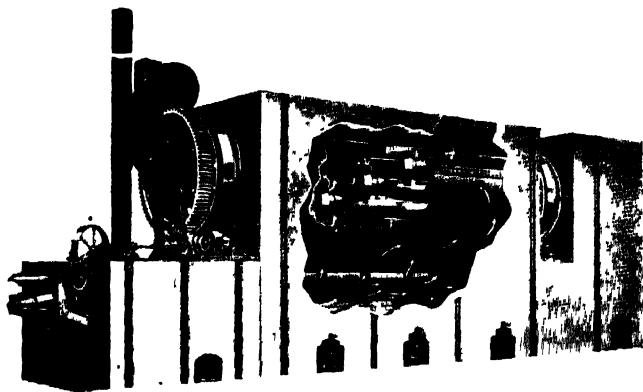


FIG. 23 —A SAND DRYER.

(By courtesy of the F. D. Cummer and Son Company, Cleveland, Ohio)

finally out on to a conveyer belt below. There are usually seven tiers of 14 pipes each, the length of the course being varied to suit the capacity desired. The two bottom tiers can be removed for cleaning when clogging occurs. A fan is provided to remove steam and dust.

The Laboratory Examination of Sands.

(75) **Microscopic Examination.**—Much information as to the purity and grading of sands can often be obtained by a simple examination with a pocket lens. An indication may be obtained by this means of the average size and shape of the grains, whilst any coating of the clear quartz crystals by clay or iron oxide may often be noted. Some of the heavier detrital minerals, particularly those of a typical colour, such as garnets, are easily found. The test is increased in usefulness if a larger magnification is used, and a microscope even of a simple type gives a great deal of information. To one familiar with geology the microscopic examination of sand samples in a suitable mounting medium such as *Canada balsam* or *clove oil* is a fruitful source of knowledge with regard to the impurities present. Properties of the minerals, such as crystalline shape, cleavage, colour, and refractive index, all serve to assist in their detection. The test is still more fruitful when applied to different fractions of the sands after sieving or washing. The separation of the heavy detrital minerals is best done by a method of floating. The specific gravity of quartz is 2.5 to 2.8, that of felspar 2.4 to 2.6, whilst the detrital minerals are, in general, heavier, ranging from 2.9 to more than 4. Any liquid of a density just a little greater than 2.8 will float quartz and allow the heavier minerals to sink. Such liquids can be obtained, as, for instance, a solution of *mercury-potassium-iodide* in water

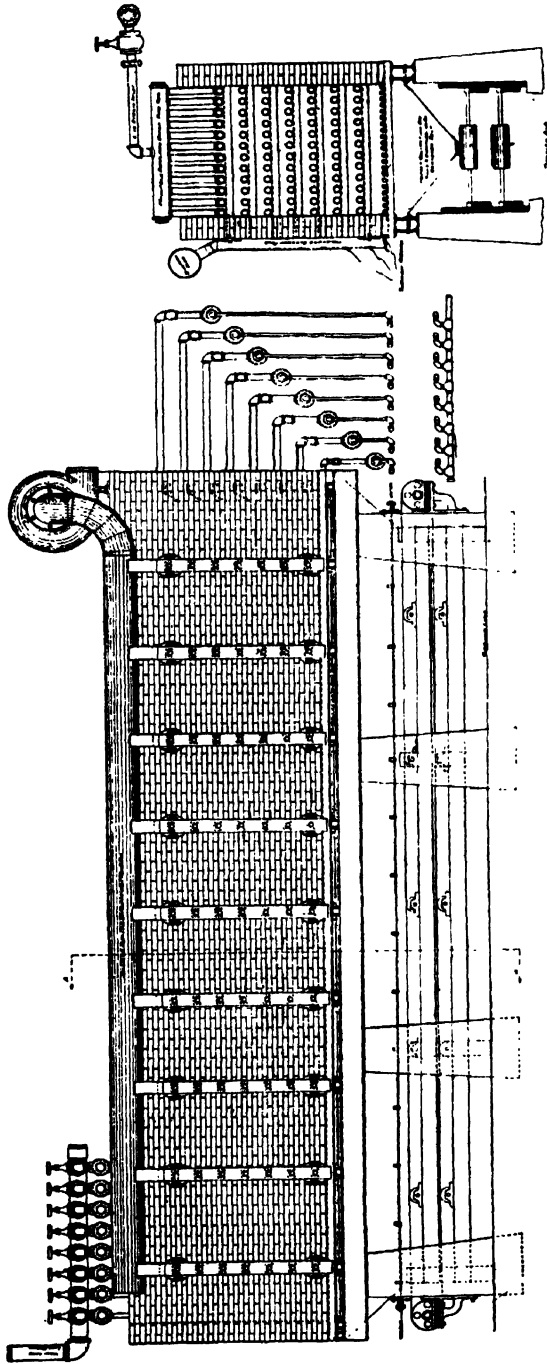


FIG. 24.—A SAND DRYER.
(By courtesy of the Lewistown Foundry and Machine Company, Lewistown, Pennsylvania.)

(which has a density of 2.8 to 3.1 according to concentration), *bromoform* with a density of 2.84, and *methylene iodide*, the density of which is 3.3.

(76) **Chemical Analysis.**—Much may be learnt concerning a sand by a study of its chemical analysis. By such means the minerals present are not estimated, but the amounts of the constituent oxides are found. The chief of these are silica (SiO_2), iron oxide (ferric oxide, Fe_2O_3), aluminium oxide (alumina, Al_2O_3), titanium oxide (TiO_2), calcium oxide (CaO), magnesium oxide (MgO), sodium oxide (Na_2O), and potassium oxide (K_2O), whilst moisture and loss on ignition (chiefly water which is not driven off at 100°C . and organic matter) are also determined. For the methods of estimation of these constituents the reader is referred to books on chemical analysis. From the values obtained, some general conclusions as to the minerals present may often be drawn. A first-class sand should, of course, have a high percentage of silica, that is, greater than 99. A large alumina content with low alkali or lime indicates generally the presence of clay, high alkalis presence of felspar, whilst calcium oxide alone usually denotes presence of limestone. The moisture should not be high since it adds to the relative cost of the sand, and is likely also to vary in amount through the consignment, a factor of importance in making up the batch. It is well to note that analytical results vary somewhat from sample to sample of the same sand, for even the best sands are not perfectly uniform in composition, whilst washing and screening improve the results obtained. The following figures for Huttons Ambo sand* serve to indicate how the same bed may give a product of varying composition:

	SiO_2 .	Al_2O_3 .	Fe_2O_3	Loss on Ignition
Sample A ..	94.28	2.54	0.30	1.34
Sample B ..	97.88	1.20	0.19	0.55

With poorer sands the differences may be still greater. Since screening and washing tends to purification, the product of any particular bed should approach constancy of composition after being submitted to this treatment.

It must be emphasised that the first step towards accurate analysis is efficient sampling, since no results will be of value if the samples treated are taken haphazardly and unsystematically.

SIMPLE TESTS FOR IRON.—Sometimes it is desirable to gain a rough idea of the amount of iron oxide in a sample of sand. Two ways are open which are easy of accomplishment. The first consists of grinding the sand to a fine powder and then igniting strongly over a good burner. The original colour of the sand is not always a good guide as to the amount of iron oxide present, for though good sands are in general almost white, yet some, such for example as Lynn sand, which have a very low iron content when washed, are of a distinctly brownish tint. On igniting, however, the intensity of the red colouration of the sand indicates to some extent the amount of contaminating iron oxide, since ignition tends to convert the iron compounds present to ferric oxide. Ignited sands low in iron content are practically white, or light grey,

* PEDDLE, *J. Soc. Glass Tech.*, 1917, 1, 47.

in colour, and sands may be compared amongst themselves by comparison of depth of tint. Exceptions to this test are sands which contain an appreciable quantity of lime, for these do not reach the same depth of colour as sands having the same iron content but less lime. The second method consists in extracting the iron with concentrated hydrochloric acid and finding the amount of iron present in solution by a colour reaction. The test is easily performed by weighing one gram of the finely ground sand into a porcelain dish and evaporating it to dryness twice with a little concentrated hydrochloric acid (5 c.c.). The sand is then moistened with a third quantity of acid, which is diluted up to 250 c.c. A portion of this (5 or 10 c.c.) is withdrawn and mixed with equal amounts of dilute hydrochloric acid and potassium sulphocyanide solutions, whereby ferric salts give a red solution of ferric sulphocyanide. The depth of colour produced in this reaction indicates the amount of iron present in the sand; good sands give only a very faint colour, but poor sands a deep red tint. In this test the materials used, water and acid, must, of course, be free from iron compounds.

HAND WASHING.—Shake some of the sand in a bottle with water, allow a few minutes for the sand grains to settle, and then decant off the supernatant liquid. Repeat the operation with fresh water until the water shows no signs of turbidity. A good sand should be practically free from silt and clay after one washing. A comparison of the colours of washed and unwashed sands often indicates whether washing will be effective in removing ferruginous impurity.

(77) **Grading.**—The best method of finding the grading of a sand is by sieving. Strictly, it does not give an analysis of the volumes of the grains, but it indicates the size of diameter in the case where the grains are perfect spheres or the length of the minor axis when, as in general, the grains are of irregular shape. In spite of this difficulty, however, sieving does serve to indicate whether the sand is uniform in grain size or not. The holes of a perfect sieve should be circular, but circular holes are difficult to punch out accurately from metal sheet when they are of small size, consequently in "nests" of sieves of this type the sieves with the smallest holes are usually made of wire-mesh. Where wire-mesh sieves are used, the size of the side of the hole is stated, but it must be borne in mind that it is really the length of diameter of the hole which decides what sizes of sand grains shall pass through. This difficulty, again, is not vital, and for practical purposes sets of sieves made completely from wire-mesh are the most common type used. Though geologists, in general, state the grading of sand in fractions of a millimetre, the common custom in England and America is to use the inch as a basis of measurement—the number of meshes per linear inch being stated. Where a sieve is a "10-mesh sieve," it is meant that it contains 10 holes or meshes per linear inch, and that these meshes are, of course, all of uniform size. Obviously the size of a single mesh will not be one-tenth of an inch, since the inch includes 10 wires as well as 10 holes, and so the true size of mesh will be something less than this, a value dependent upon the diameter of the wire of which the sieve is composed. To obviate this difficulty a set of sieves has been designed by the Institute of Mining and Metallurgy, in which the diameter of wire

of any sieve is exactly equal to the size of the mesh. In this set of sieves the 10-mesh sieve will have a series of uniform square holes of 0.05 inch side. The full set of I.M.M. sieves is 13 in number, arranged as follows:

<i>Mesh, Apertures per Linear Inch.</i>	<i>Size in Inches.</i>	<i>Size in Millimetres.</i>
10	0.0500	1.276
12	0.0416	1.056
16	0.0312	0.792
20	0.0250	0.635
30	0.0166	0.421
40	0.0125	0.317
50	0.0100	0.254
60	0.0083	0.211
70	0.0071	0.180
80	0.0062	0.157
90	0.0055	0.139
100	0.0050	0.127
120	0.0042	0.107

Comparison with the metric grading indicates that gravel and coarse sand will not pass the 12-mesh sieve, whilst only superfine sand, silt, clay and mud will pass through the 120-mesh sieve. Good sands have, as we have seen, closer limits still, and, in general, the bulk of the sand will rest on two or at most three consecutive sieves. As examples, in a sample of Fontainebleau sand 80 per cent. passed through the 50 sieve but failed to pass through the 80 sieve, and in a sample of Lynn sand 33 per cent. was between 50 and 60-mesh size, and 45 per cent. between 60 and 80-mesh. It is not necessary to use the whole of the set of sieves in the ordinary way, and a selection of them may be made, such, for instance, as 10, 20, 30, 40, 50, 60, 80, 100, and 120. For simplicity of interpretation a graphical method of representation is recommended. Instead of plotting the size of mesh as abscissæ and the single percentages as ordinates, a method giving a curve with more or less of a peak, it is found preferable to plot cumulative percentages as ordinates. The cumulative percentage of a sand of greater diameter than any particular size of mesh is the *total* percentage of sand which will not pass through this mesh. To make the point clear, take as an example Hutton's Ambo sand, for which the following results have been obtained by sieving:

<i>Mesh of Sieve.</i>	<i>Total Weight of Sand Used = 100 Grams. Weight of Sand Left on Sieve (Grams).</i>
10	0
20	0.1
30	1.0
50	12.7
60	26.2
80	40.9
90	3.9
100	3.3
120	5.9
Passing 120	6.0

The cumulative percentages will be:

<i>Mesher per Inch.</i>	<i>Cumulative Percentages.</i>
10	0
20	0.1
30	1.1
50	13.8
60	40.0
80	80.9
90	84.8
100	88.1
120	94.0
Less than 120	100.00

The curve for this sand is given in Fig. 25. It will be seen that the great bulk of the sand lies between 30 and 80-mesh, or 0.421 mm. and 0.157 mm. diameter. The ideal sand would have a perfectly uniform grain, hence its cumulative percentage curve would be a vertical line, such as **XY**. The further the curve departs from the vertical the less even is the grading of the sands. Fig. 25 gives the grading curves of a number of sands and crushed rocks. It will be seen that the former are the more evenly graded.

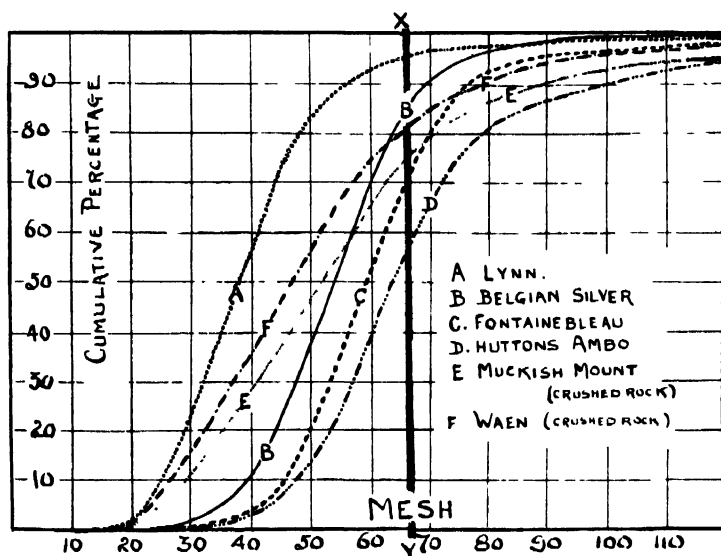


FIG. 25.—GRADING CURVES OF SANDS AND CRUSHED ROCKS.

(78) **The Chemical Composition of Sands.**—In Table XXIV. are given typical chemical compositions of some of the most widely-used sands and crushed rocks employed in the glass industry:

TABLE XXIV.—THE CHEMICAL COMPOSITION OF SANDS

Sand.	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	Alkalis.	Loss on Ignition.	Remarks.
BRITISH:								
Lynn (Boam's double-washed)	98.82	0.56	0.06	0.16	0.02	—	0.33	—
Aylesbury	98.70	0.42	0.20	0.40	0.10	—	—	—
Leighton Buzzard ..	98.60	0.50	0.14	0.50	0.29	Trace	—	—
Waeln	98.63	0.41	0.03	0.16	—	0.26	0.28	Crushed rock
IRISH:								
Muckish Mt.	99.55	0.17	0.02	0.20	Trace	—	0.16	Crushed rock
FRENCH:								
Fontainebleau	99.50	0.23	0.04	—	—	—	0.22	..
DUTCH	99.63	0.35	0.03	0.08	Trace	—	0.19	—
BELGIAN	98.64	0.63	0.06	0.31	0.13	0.45	0.12	—
GERMAN:								
Hohenbocka	99.70	0.35	0.05	—	—	—	0.10	—
Nievelstein	99.97	—	0.01	0.01	0.01	—	—	—
Lippe	99.88	0.18	0.02	—	—	—	0.21	—
UNITED STATES:								
Berkeley Springs, W. Va.	99.65	0.11	0.02	0.12	Trace	—	0.23	} Crushed rocks
Wedron Silica Co., Ottawa, Ill.	99.58	0.12	0.02	0.13	Trace	—	0.17	
Cheshire, Mass. ..	99.00	0.30	0.03	0.15	—	—	0.21	
Tavern Rock Sand Co., St. Louis	99.03	0.23	0.02	0.21	0.05	—	0.35	

(79) **Boric Oxide** (Formula, B_2O_3 . Molecular weight, 70).—Boric oxide is obtained by heating boric acid. The ordinary boric acid is *ortho-boric acid*, H_3BO_3 , which loses water at $100^\circ C.$, giving *meta-boric acid*, HBO_2 . At $140^\circ C.$ a variety of the acid—*pyro-boric* or *tetra-boric acid* ($H_2B_4O_7$)—is formed, and finally on more strongly heating, boric oxide itself is obtained. Though boric oxide may be used, it readily absorbs moisture in the air to re-form boric acid, causing its composition to be uncertain, hence boric acid, or in some cases borax, is preferable as a batch constituent.

BORIC ACID (*Orthoboric acid*. Formula, H_3BO_3 . Molecular weight, 62).—The acid is found free in nature in many volcanic districts, as, for instance, in central Italy, where, in Tuscany, it is produced on a large scale. American sources occur in Nevada, California, Nova Scotia, and the west coast of South America. The boric acid from Tuscany is always associated with impurities both soluble and insoluble, the acid content of the commercial product being 75 to 89 per cent. A more pure acid may be obtained by treating a hot aqueous solution of borax with sulphuric acid, when, on cooling, boric acid separates out and may be purified by recrystallisation. The boric oxide content of orthoboric

acid is 56.45 per cent., and there is 43.55 per cent. of water. As compared with borax the acid is expensive, and the former is generally employed where the composition of the glass allows of the inevitable addition of sodium oxide which occurs when borax is used.

BORAX (*Sodium pyroborate*. Formula, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$. Molecular weight, 382).—The above is the common form of commercial borax, though a *penta-hydrate* ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ —Molecular weight, 292), and the *fused borax* ($\text{Na}_2\text{B}_4\text{O}_7$ —Molecular weight, 202), are also sometimes used. Borax is the salt of pyroboric acid, and is found naturally as the mineral Tincal in Thibet and California. Its chief source is other natural borates, of which those of lime are the most common. Bolivia provides a large amount of these. Of natural salts, *Borocalcite* ($\text{CaB}_4\text{O}_7 \cdot 6\text{H}_2\text{O}$) and *Colemanite* ($\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$) are used in manufacturing borax. One method of production is to boil the powdered mineral with a slight excess of an aqueous solution of sodium carbonate. Calcium carbonate is deposited as a mud, and on recrystallising the clear solution borax is obtained.

The percentage composition of borax is sodium oxide 16.2 per cent., boric oxide 36.6 per cent., water 47.2 per cent., the figures applying to the crystallised deca-hydrate. The use of borax necessitates the adjustment of the amounts of the remaining sodium compounds in the batch. The chief impurities of boric acid and borax are alumina, lime, magnesia, and the alkalis, occurring as the silicates, sulphates, and carbonates.

(80) **The Properties of Boric Acid Glasses.**—Boric acid and borax act as fluxes, but are less powerful in this respect than sodium carbonate. They readily dissolve many colouring oxides, and boro-silicate glasses are used for the production of certain colours (a few colours are not readily developed in presence of boric oxide). One of the chief effects of boric acid as a constituent of glass is to decrease the coefficient of expansion, and this, coupled with the fact that the toughness is also increased, renders boro-silicate glass of a high thermal endurance. One important use of the glass is for articles which have to undergo sudden changes of temperature, such as lamp chimneys, thermometer tubes, and cooking ware. In such glasses the 'alkalis, which do not favour thermal endurance, are kept as low as possible, whilst favourable oxides such as zinc oxide or alumina are added in many cases. Small amounts of boric oxide render glass very resistant to attack by water, one per cent. greatly improving lead glass in this respect. The increase of thermal endurance and of chemical resistance makes boro-silicate glasses useful for chemical ware.

The optical properties, refractive index and dispersion, of a number of boro-silicate glasses render them important for certain optical purposes.

(81) **Phosphoric Oxide** (Formula, P_2O_5 . Molecular weight, 142).—*Calcium phosphate*, $\text{Ca}_3(\text{PO}_4)_2$, is often used as a source of phosphoric oxide. Its chief use, however, is as an opaliser, and it will be described under the heading of colouring substances. As a source of the oxide it is better to use *sodium phosphate*, $\text{Na}_2\text{H}(\text{PO}_4) \cdot 10\text{H}_2\text{O}$. Phosphoric oxide is sometimes found in table-ware—one of the above phosphates

having been added to the glass to give it a brighter appearance. The oxide is a constituent of certain optical glasses, phosphate crowns, of which it may form up to 60 per cent. Phosphate glass lenses are readily attacked by the atmosphere and weathering agents, and must be placed in protected parts of an optical system.

(82) **Arsenious Oxide** (*Formula, As_2O_3 . Molecular weight, 396*).— Since arsenious oxide is an acidic oxide it is included here, but it is commercially supposed to be valuable as a fining agent, flux, and de-colouriser (see pp. 110, 112, and 133).

APPENDIX.

1. In connection with the introduction of boric oxide into glass it may be mentioned that a further commercial form of borax exists—namely, *calcined* borax. This form contains an amount of water which depends somewhat on the degree of calcination. At 50° C. $Na_2B_4O_7 \cdot 10H_2O$ loses five molecules of water; at 80° C. dehydration to $Na_2B_4O_7 \cdot 2H_2O$ occurs, and at 200° C. $Na_2B_4O_7 \cdot H_2O$ is produced. A temperature of 350° to 400° C. to be required in order to remove the remaining molecule of water. A sample actually used in the Department of Glass Technology contained about 21 per cent. of water.

2. Since paragraph 80 was written it has been proved that not only are maximum and minimum values for the coefficient of thermal expansion, density, and refractive index found to occur in glasses containing certain proportions of boric oxide, but also for durability. Accordingly, any attempts to improve heat-resisting glasses or chemical glassware by the introduction of ever-increasing percentages of boric oxide are doomed to failure.*

* See CAUWOOD and TURNER, *J. Soc. Glass Tech.*, 1918, **2**, 233; also TURNER, *J. Amer. Cer. Soc.*, 1924, **7**, 313.

CHAPTER VIII

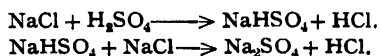
THE RAW MATERIALS USED IN GLASS MANUFACTURE

—continued

(B) Basic Oxides.

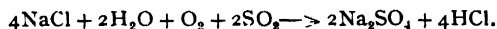
(83) **Sodium Oxide** (*Formula, Na_2O . Molecular weight, 62*).—The most widely occurring natural sodium compound is common salt, sodium chloride. It occurs in sea-water and as rock salt in enormous amounts. From the rock salt beds it is pumped out as brine and crystallised. It is unfortunate that this substance cannot be used as a source of sodium oxide. The reasons which prevent the use of salt as a batch constituent are the facts that it is volatile at white heat and is not decomposed by silica except in presence of steam. Attempts have been made to employ it directly in glass manufacture, usually associated with slaked lime, but without success. It must therefore, before it can be used, be converted into other sodium compounds which more readily react with silica. The two sodium compounds which are commonly used are saltcake (sodium sulphate) and soda ash (sodium carbonate). Undecomposed sodium chloride in glass may produce an opalescent effect, and it is chiefly for this purpose that the substance is added to glass batches.

(84) **Sodium Sulphate** (*Saltcake. Formula, Na_2SO_4 . Molecular weight, 142. Melting point, 885°C .*).—This substance does not occur nearly so extensively in nature as sodium chloride, but deposits are found in Spain, Peru, Hungary, Siberia, and the western States of America. Glauberite, a double sulphate of sodium and calcium, also occurs in many places, and has been suggested as a substitute for saltcake itself. The great bulk of saltcake, however, is made directly from common salt. The most usual method of converting the chloride to sulphate is the Leblanc process, in which salt and sulphuric acid are heated together with evolution of hydrochloric acid. The action commences at a low temperature, but it is only completed at a dull red heat. It is usually taken in two stages represented by the equations—



The first stage results in the decomposition of more than 50 per cent. of the salt, the actual amount depending on the temperature, and is performed in shallow iron pans nine to eleven feet in diameter and about two feet deep. Above the pan is a dome of acid-resisting brick. The second portion of the action takes place in roasters, either open

reverberatory furnaces or muffles. In some places the operation is carried out in one stage only. On the Continent special saltcake is made for glassmakers, in the manufacture of which lead-lined pans are used in the first portion of the process. Very careful heating is required in such cases, but the product is much freer from contamination by iron. A direct process, that of Hargreaves-Robinson, combines the manufacture of the sulphuric acid and its decomposition of the salt into a single process. Gases from pyrites or "spent oxide" burners, together with steam and air, are passed through a series of cast-iron cylinders containing salt. The fresh gases meet the salt which has been longest exposed. The reaction takes place at 500° to 550° C., and is expressed by the equation—



The action is exothermic and does not require a large consumption of fuel. Good quality saltcake made by this process is practically iron-free. In all processes the quality of the product depends, of course, on the purity of the salt used. The total content of sodium sulphate should reach 95 per cent. Impurities most generally found are sodium chloride, free acid (really sodium bisulphate), iron, insoluble matter, and moisture. For use in glass manufacture Springer gives the limits of the impurities as sodium chloride 1 per cent., free acid 2 per cent., insoluble matter 1 per cent. (of which the calcium sulphate content should be small, since this tends to give gall). The iron, which occurs chiefly as soluble ferrous sulphate and to a less extent as ferric oxide in the insoluble portion, should be small in amount for the best type of glass. Plate glass, for which saltcake is usually used, requires a good quality of the substance, but for common bottles the iron content is not of such great importance. The limit for plate glass is about 0.02 per cent. Fe_2O_3 . Good quality saltcake made by the Hargreaves-Robinson process is, as we have seen, almost free from iron, whilst the product from the lead pan process contains 0.01 to 0.03 per cent. Fe_2O_3 . When made by the iron pan process the ferric oxide content varies, according to Springer, from 0.07 to 0.13 per cent., though higher values are common. The moisture content of freshly prepared saltcake is low, but the substance fairly readily combines with water, tending to give the hydrated Glauber's salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$). This causes a balling together of the mass into hard lumps, particularly in a moist atmosphere. The moisture content of samples of saltcake will therefore increase with standing, more particularly on the surface of the mass. If large quantities are stored they should be kept in a dry place, for if much hydration occurs it may be necessary to grind up the hard rock-like product in order to obtain efficient batch mixing.

Several commercial processes give saltcake as a by-product of sufficient purity for common types of glass. It is obtained in good quality at Stassfurt as a by-product of the potash industry. Nitre cake, the residue from the manufacture of nitric acid by the action of sulphuric acid on sodium nitrate, is also of fairly good quality, but may contain a rather large amount of free sulphuric acid. A third type results from the manufacture of potassium dichromate. It generally contains from

1 to 3 per cent. of sodium chromate, and is yellow in colour, although samples of green "chrome-salt" may now be obtained in which the chromium is in a lower state of oxidation. Chrome saltcake can only be used for green bottles, its chief disadvantage in this respect being the irregularity of the chromium content.

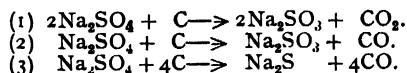
TABLE XXV.—ANALYSES OF SALTCAKES.

Constituents.	<i>Hargreaves- Robinson Saltcake.</i>	<i>Leblanc Saltcake.</i>			<i>First Quality Stassfurt Saltcake.</i>	<i>Chrome Salt.</i>
		1	2	3		
Na ₂ SO ₄ ..	0.8	96.24	94.40	88.36	97.0	96.09 (by difference)
NaCl ..	0.2	0.26	2.45	0.31	1.6	Trace
H ₂ SO ₄ ..	0.3	1.32	1.23	0.84	—	Trace
CaSO ₄ ..	—	—	—	—	1.1	0.68
CaO ..	—	—	0.82	—	—	—
Total Fe ₂ O ₃	0.076	0.48	0.26	0.15	0.04	0.06
Al ₂ O ₃ ..	—	—	0.17	—	—	1.44
Na ₂ CrO ₄ ..	—	—	—	—	—	1.53
Insoluble matter	1.42 (with CaSO ₄)	1.09	0.54	0.36	0.3	0.18
Moisture ..	—	0.89	—	5.67	—	—
Loss on igni- tion	—	2.36	1.55	10.93	—	—

Pure anhydrous sodium sulphate contains 43.7 per cent. of sodium oxide.

The reaction between saltcake and silica only occurs at very high temperatures, being incipient at about 1220° C., and it is very slow under 1350° C. Some means must therefore be employed for increasing the speed of the reaction in actual practice. It is found that sodium sulphite Na₂SO₃ reacts much more readily than saltcake. By "reducing" the saltcake, that is, by removing one atom of oxygen per molecule, the resultant is sodium sulphite, and this action takes place at high temperatures where unburnt furnace gases come into contact with the material. In tank furnaces where the atmosphere is reducing much of the saltcake is so decomposed, but even then it is better to add some reducing agent with the batch, carbon in some form being so used. In pot furnaces no reduction by the gases can take place and the carbon added must be sufficient to secure full reduction. The carbon is added as best anthracite or good coal, well ground up, and mixed, preferably with the saltcake, before the latter is added to the batch.

Reactions which may occur between carbon and sodium sulphate are:



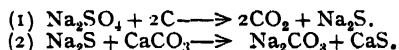
The second of the above reactions most nearly represents the usual course of the reduction, and in this 12 parts by weight of carbon are

needed for 142 of sodium sulphite—*i.e.*, 8.5 per cent. Usually carbon to the extent of 5 per cent. by weight of the saltcake is added and is sufficient.

Unreduced saltcake is liable to remain on the surface of the glass in the form of a pool of "salt," "flux," or "gall." If carbon is in excess it is liable to cause foaming of the metal, especially where the carbon is finely divided. Any excess carbon left in the glass produces in it an amber colour, although not all excess carbon will remain behind, for some will burn off in the melting process.

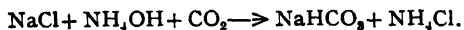
(85) **Sodium Carbonate** (*Soda ash, alkali. Formula, Na_2CO_3 . Molecular weight, 106.*)—Naturally occurring sodium carbonate is found in the alkaline lakes of Nevada and South California. The product from this district receives the name "natural soda," or "trona," and has a composition of $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot \text{H}_2\text{O}$. A very large deposit, thirty square miles in extent, occurs at Magadi, 60 miles south of Nairobi, in British East Africa. This deposit is crystalline in character, giving, when calcined, a product containing 99 per cent. of sodium carbonate. The working of this deposit is carried out by the Magadi Soda Co., Ltd.

The chief commercial processes for the production of soda are two methods by which it is prepared from common salt—the **LEBLANC** process and the **SOLVAY** process. The Leblanc process is a continuation of the method previously described for sodium sulphate, in which the saltcake so obtained is heated with limestone and coal in a long reverberatory furnace, when the following reactions take place:



The mass is raked, with stirring, from the cold to the hot end of the furnace, where it reaches a temperature of about 1000°C . A resulting cake dark in colour due to the excess coal is obtained, hence it is named "black ash." This ash is carefully lixiviated with water, the liquor so obtained containing the sodium carbonate, with a number of sodium compounds such as caustic soda, sodium sulphide, sodium thiosulphate, etc. After settling, the liquid is purified by one of several methods, whereby the amount of the impurities is diminished, and the solution is then evaporated in cast iron pans. By this means "soda salt," ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$), crystallises out. The product on calcination yields "soda ash."

The Solvay, or Ammonia-Soda process, depends upon the fact that when a solution of sodium chloride is saturated with ammonia and carbon dioxide is passed in, the sparingly soluble sodium bicarbonate is precipitated, whilst ammonium chloride is left in solution. The reaction taking place is represented by the following equation:



In practice, brine is saturated with ammonia gas. The cooled ammoniacal liquid is then charged with carbon dioxide under moderate pressure in carbonating towers, tall cast-iron cylinders divided by plates with central openings over which are dome-shaped diaphragms pierced

with many small holes. The bicarbonate is filtered and washed in the cold with water. In practice from 30 to 40 per cent. excess of sodium chloride must be used, and also excess of carbon dioxide. There is thus a considerable loss of sodium compounds in the mother liquor, whilst all the chlorine is lost except for such use as can be made of calcium chloride. The ammonium chloride is treated with lime, and the ammonia liberated is again used. Calcination of the bicarbonate yields sodium carbonate, and carbon dioxide which is used once more in saturating the ammoniacal brine. Roasting usually takes place in two stages, in the first of which ammonia is driven off and about 75 per cent. of the excess carbon dioxide, after which further heating at higher temperature completes the decomposition. The second stage may be done continuously in a pan provided with agitators, when a finely-divided, dusty product results known as "*light ash*." If calcined at a higher temperature and in contact with furnace gases a denser product, "*heavy ash*," is obtained. A litre jar well shaken down will hold 900 to 1,000 grams of light ash and about 1,500 grams of heavy ash. There is no difference in quality between the two products, but the light ash costs more for packing and transport, and in the glass furnace is not so good, owing to its liability to be carried away into the flues by draughts. It is sometimes a source of confusion that Leblanc soda is heavy ash, and hence light ash (or ammonia soda ash) has been preferred on account of its superior quality. The heavy ash from the Solvay process is equally superior to the heavy Leblanc ash. The Solvay process, which is the more recent method, is, on account of its simplicity and the purity of the product, gradually displacing its rival, and, indeed, but for the hydrochloric acid obtained in the first part of the Leblanc process, the latter would probably have been discarded long ago. The anhydrous sodium carbonate contains 58.5 per cent. of sodium oxide, and is referred to in the trade as 58 per cent. ash. Its melting-point is 810°C . Two classes of product are sold, refined soda and calcined soda. The chief impurities in commercial soda are sodium chloride, sodium sulphate, lime, iron oxide, and insoluble matter, but they are usually present in small quantity. In addition, Leblanc soda contains some caustic soda and sulphur compounds, whilst Solvay soda may contain bicarbonate. As limits for the various impurities Springer gives the following values: Caustic soda up to 5 per cent. is not harmful. Sodium sulphate only occurs to about 0.1 per cent. in Solvay soda, but is 0.5 to 1.0 per cent. of the best Leblanc soda, and poorer types may contain 8 per cent. or more. Large amounts of sulphate should not be present in soda used for crystal glass, since it tends to produce gall. Sodium chloride forms only 0.25 to 0.5 per cent. of good Leblanc soda and 0.5 to 2.5 per cent. of Solvay soda. It mostly volatilises in melting, and so is worthless as a glass-forming compound, but it may result in the formation of gall. Refined soda should contain no insoluble matter, calcined soda not more than 1.5 per cent. In good soda the iron content should not exceed 0.02 per cent., particularly for white glass.

It is important that soda ash should be kept in a dry place, since it readily absorbs moisture and carbon dioxide, reverting to sodium bicarbonate. If stocked for a long time, regular determinations of the moisture

content should be made and the batch adjusted accordingly. The compositions of a number of samples of commercial soda ash are given in Table XXVI.

TABLE XXVI.—THE COMPOSITIONS OF SAMPLES OF SODA-ASH.

Constituent.	Leblanc Soda.*	Ammonia Soda.†		Magadi Soda	
	1	1	2	1	2‡
Na ₂ CO ₃	96.5	98.96	99.08	68.22	69.67
NaOH	0.1	—	—	—	—
NaCl	0.5	0.81	0.85	1.36	0.36
Na ₂ SO ₄	1.1	0.10	—	—	—
Fe ₂ O ₃	{ 0.5 }	—	—	0.23	{ 0.04 }
Al ₂ O ₃	—	—	—	—	—
CaO	—	—	—	—	—
MgO	0.2	—	—	—	—
SiO ₂	1.1	—	—	—	0.07
Insoluble matter	—	—	—	0.36	—
Volatile matter	—	—	—	28.83	15.57
CaCO ₃ }	—	0.13	0.07	—	—
MgCO ₃ }					
Fe ₂ O ₃ }					

(86) **A Comparison of Sodium Sulphate and Sodium Carbonate as Batch Constituents.**—The difference in price, originally, was so much in favour of the sulphate, that, when the higher furnace temperatures necessary for saltcake batches were made possible by the introduction of the Siemens furnace, soda-ash began to be displaced by saltcake. The Solvay process, on its introduction, reduced the price of soda-ash and caused a reversion, to some extent, to its use.

It must be borne in mind, in a comparison of prices, that soda-ash gives 58.5 per cent. of sodium oxide, saltcake only 43.7 per cent., so that only two-thirds of the former is needed to produce the same amount of the oxide. Again, the temperature required for founding a soda-ash batch is less, Dralle maintaining that a saving of 30 per cent. of fuel is possible. Moreover, the life of the furnace is lengthened, due partly to the lower temperature at which it works and also to the less active attack upon the refractories by soda-ash than by saltcake. Other factors in favour of soda-ash are the great loss of sulphur occasioned by the use of saltcake, and the difficulty occasioned by turning into the air so much strongly acid fume. Further, saltcake frequently needs the presence of carbon as a reducing agent; inaccurate regulation of the quantity of carbon used causes difficulty—*i.e.*, excess may give an amber colour to the glass, whilst a deficit tends to produce "gall." Since glass high in alkali tends to dissolve saltcake more readily, cooling, such as occurs at the working end of the tank, may cause the sulphate to separate out again in the form of sulphate stones, particularly if the temperature is appreciably reduced.

On the other hand, difficulties are occasioned by the use of soda-ash

* Thorpe's *Dictionary of Applied Chemistry*.

† Bernburger Sodafabrik.

‡ Gordon Salamon (recalculated).

alone. The reaction between the carbonate and the rest of the batch is rapid at low temperatures, being completed at 1200°C . The rapid evolution of gas and rush of the bubbles drives some of the fine sand particles to the surface of the melt into a region which contains little free alkali and the silica consequently escapes attack and forms a scum. The reaction between the saltcake and other materials is much less rapid until higher temperatures are reached, being especially active at 1370°C . Consequently an appreciable amount of flux remains in the upper layers at higher temperatures, and is capable of attacking any silica which may rise into these layers. Gelstharp* states that for the production of glass with more than a certain proportion of lime (above one molecule to two molecules of soda), soda-ash cannot be used alone, but the batch must contain some saltcake to prevent the formation of scum.

Hodkin and Turner† have also observed that scum is formed in glasses made entirely from soda-ash. The method at present adopted in practice is to introduce a small amount of saltcake into soda-ash batches in order to obviate this difficulty.

In regard to the rate of melting of soda-ash and saltcake batches, Hodkin and Turner have concluded that where the two are melted at the same temperature much depends upon the form in which the calcium oxide is supplied—that is, whether it is added as limestone, quicklime, or slaked lime.

Gelstharp is of the opinion that "saltcake" glass for use in plate form is often less reamy, and that "soda-ash" glass is more difficult to obtain free from seed, fining being more efficient in the former due to the evolution of sulphur dioxide at high temperatures.

Glass from saltcake is generally held to be "sweeter" for working than glass for which soda-ash is used, this not implying that it is softer, but that it works and shapes somewhat better than the soda-ash glass. This effect may be due to the fact that some saltcake is dissolved in the glass and so affects its properties. Frink‡ regards the sulphate glass as being less viscous at about 850°C . than soda-ash glass of similar composition, whilst it also is more likely to be wavy and cordy, due to impressed marks, at temperatures below 945°C . General opinion has been that sulphate glasses are stronger and more resistant than "alkali" glasses, whereas the latter are less brittle and more suitable for lamp working. Springer§ came to the conclusion that such was not the case, these results only occurring when soda-ash and saltcake are used in equal weights and not in equi-molecular amounts. Frink states, on the other hand, that saltcake glasses are harder, of greater strength, and of higher softening point than soda-ash glasses.

It is asserted by some authorities that the blue tint frequently obtained in the glass is due generally to particles of colloidal sulphur from the saltcake used. Evidence for this is contradictory since, in the case of high alkali glasses, a bluer tint has generally been observed in those which have been made with soda-ash alone than in those made with saltcake.

(87) **The Properties of "Soda" Glasses.**—Sodium silicate is an important constituent of most common glasses, but since the resultant

* *Trans. Amer. Cer. Soc.*, 1914, 16, 109.

† *J. Soc. Glass Tech.*, 1921, 5, 188.

‡ *Trans. Amer. Cer. Soc.*, 1909, 11, 296.

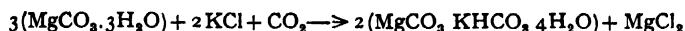
§ *Ker. Rundschau*, 1907.

glass when soda and sand alone are used is soluble, it is only employed along with a basic oxide such as lime or lead oxide to impart stability. Soda is a flux and a high soda content in soda-lime glasses allows more ready melting of the glass. Glasses rich in soda are softer and can be blown into shape more easily. The viscosity range of soda-lime glass is lengthened with increase of sodium oxide, allowing the glass to be worked over longer ranges of temperature, and making such glass suitable for use in machines where it becomes quickly chilled—such as rapid automatic machines in which the glass comes in contact with large masses of heat-conducting metal work (see also Molecular Composition of Glass, p. 60). Increase of soda also gives the glass a smaller heat conductivity, which results in a slower rate of cooling and allows a longer time between the ejection of the article from the machine and the placing of it in the lehr. High soda glass has a lower annealing temperature than high lime glass.

On the other hand, a large soda content produces a large coefficient of expansion, and a reduced tensile strength and elasticity, factors which militate against the thermal endurance of the glass. Above all, high alkali glass has a decreased durability, and is more readily attacked by the atmosphere and liquids with which it comes in contact than glass low in soda. When the amount of the oxide exceeds 18 per cent., glasses are of such low durability that they are attacked quickly on exposure, becoming dirty and dull in appearance, and containers made from such glass are likely to contaminate any liquids which they contain.

(88) **Potassium Oxide** (*Formula, K_2O . Molecular weight, 94*).—When sodium oxide is replaced by potassium oxide, the resultant glass has a greater brilliance and a better colour, is generally harder and possesses a higher melting-point than the soda glass. The latter, however, does not require so high a temperature to found, and at ordinary temperatures of working is less viscous. The potassium oxide is supplied as potassium carbonate and potassium nitrate. Although potassium compounds occur fairly largely in nature, the great bulk of these are silicates, of which feldspars and micas are the most important. Orthoclase feldspar has the general formula $(KAlSi_3O_8)$, with, theoretically, a little over 16 per cent. of potassium oxide, whilst micas are silicates of potassium, sodium, aluminium, and iron. There are no practicable methods, unfortunately, by which the silicates may be decomposed, and we are driven to other sources for our supply of potash compounds. There are two large mineral sources of potassium compounds at present known, those at Stassfurt in Germany and those near Mülhausen in Upper Alsace in France. The former beds contain the following potassium compounds: *syilvine* (KCl), *carnallite* ($KCl \cdot MgCl_2 \cdot 6H_2O$), *kainite* ($K_2SO_4 \cdot MgSO_4 \cdot MgCl_2 \cdot 6H_2O$), and *leonite* ($K_2SO_4 \cdot MgSO_4 \cdot 4H_2O$). From these deposits the carbonate is mostly prepared by the Leblanc method previously described. The Solvay process cannot be used, since potassium bicarbonate is appreciably soluble in water. To obtain a purer product the potash is redissolved by the aid of steam and crystallised. The hydrated carbonate, $K_2CO_3 \cdot 3H_2O$, is occasionally used for flint glass making. In another process which is used, the chloride is decomposed by magnesium

carbonate and carbon dioxide in solution, with the formation of a double potassium-magnesium carbonate, which is precipitated and removed—viz ,



The double salt decomposes on treatment with water, the magnesium-carbonate being precipitated. This is filtered off, and evaporation of the solution so obtained gives a good quality of potassium carbonate.

The Alsace deposits are the largest known, and are composed of two beds, the upper averaging 35 per cent. and the lower 30 per cent. of potassium chloride. Altogether, the deposits total about three hundred million tons.

In America some potash is obtained by evaporation of the water from several lakes in Nebraska, California and Utah.

Potassium compounds are found in the ashes of wood and land plants. Lixiviation of these ashes with water containing a small quantity of lime, and subsequent evaporation and calcination, gives a product known as "pot-ash." This process is carried on in Russia and in America, where a more purified product is given the name "pearl ash." A further vegetable source, chiefly French, is beetroot molasses.

As compared with sodium carbonate, the amount of potash obtained is small and much more expensive. Consequently the use of potash is restricted to special glasses such as lead crystal glasses, where high dispersion is an essential consideration, "Bohemian" glasses (potash-lime-silica), where high softening point is needed, and in optical glasses. The anhydrous salt is highly deliquescent; it very rapidly forms a pasty, even wet mass on exposure, and finally a solution.

TABLE XXVII—ANALYSES OF POTASSIUM CARBONATE.

Constituents.	Leblanc Potash.*		Magnesia Potash †	Molasses Potash. ‡		Wood Potash. ‡		
	Commercial.	Refined.						
K ₂ CO ₃ ..	85 to 92	92 to 98.5	99.45	1	2	1	2	3
Na ₂ CO ₃ ..	"	2.5 ,, 0.5	0.05	54	83	77.5	69.61	68
KCl ..	2.5 to 0.5	2.5 ,, 0.6	0.06	20	11	2.86	3.09	5.8
K ₂ SO ₄ ..	10 ,, 2	3.0 ,, 0.4	0.02	19	2	2.65	2.09	8.1
H ₂ O ..			0.40	3	1	11.65	14.11	15.3
Insoluble ..			—	3	3			
				1	—			

(89) **The Effect of Potash in Glass.**—As in the case of sodium compounds the potassium compounds act as a flux, the resulting potassium silicate having similar properties to those of sodium silicate. The rate of melting and fining of potash glass, however, is less than that of soda glass, and the product is more viscous. Potash glass is more free from

* Leblanc potash always contains sodium salts. It is customary to state the percentage of potassium carbonate in the material used—i.e., 92 per cent. potash.

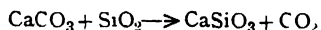
† SPRINGER.

‡ THORPE: (1) Canadian, (2) Russian, (3) United States.

the green colour due to ferrous compounds than is soda glass, particularly when used in conjunction with lead oxide. It is therefore more easily decolourised and is also used in the production of many coloured glasses. The hardness of potash glass is greater than that of soda glass. In regard to solubility, potash-lime glass dissolves less readily than lime glass of the same percentage composition containing soda, whilst a similar glass containing the two oxides in equal proportions by weight is less soluble than either. Weight for weight of alkali, potash-lime glass has not so great a refractive index or density as the soda-lime glass. In the case of lead glasses, Peddle* states that when equal weights of the oxides are used the soda glasses have a higher density and refractive index, the refractive index of the potash glass being only slightly larger when equi-molecular amounts of the two oxides are employed. As with lime glasses a glass containing a mixture of the two oxides is much more resistant than one in which either oxide occurs alone.

(90) **Calcium Oxide** (*Formula, CaO. Molecular weight, 56*).—In addition to the alkaline oxides a second basic oxide must be used to give stability and resistance to the glass. The most commonly used oxide for this purpose, not only because it gives a stable and resistant glass, but also because its derivatives occur widely in nature, is calcium oxide or lime.

Calcium Carbonate (*Formula, CaCO₃. Molecular weight, 100*).—Calcium carbonate, the most generally used lime derivative, is found in several forms—namely, as transparent crystals of *Iceland spar*, as opaque crystals of *calcite*, *calcspar*, or *limespar*, as *marble* (minute grains of calcite), as fibrous crystals of *satin-spar*, and as the less pure varieties of *limestone and chalk*. Limestone rocks are abundant, having been formed beneath the waters of many ancient seas. Sea-shells are also composed chiefly of calcium carbonate. The carbonate is readily decomposed even by dilute and weak acids, and in the glass furnace it is decomposed, even at relatively low temperatures, by silica to give calcium meta-silicate:



Limespar is a fairly pure variety of the substance and is used, in general, where a better quality of product is desired.

The chief impurities in limespars and limestones are iron oxide, alumina, magnesia, and residue insoluble in acid, the first being the most deleterious. Since calcium carbonate forms generally less than 20 per cent. of an ordinary batch, the effect of any iron present in it will not be so important as that of iron in the sand or alkali. But even so, for good glass the iron content should be kept low. Good limespars can be fairly easily obtained with less than 0.2 per cent. of ferric oxide. Alumina itself, as in the case of sand, is not detrimental, but usually high alumina content coincides with high iron oxide content. Practically all limestones contain magnesia, which in small quantities has no harmful effect. Some limestone rocks contain very large amounts of magnesium carbonate; indeed, the carbonates of lime and magnesia are occasionally

present in such rocks in practically equi-molecular proportions. The resulting mineral, which has the formula $\text{MgCO}_3 \cdot \text{CaCO}_3$, is known as *dolomite*, and contains about 21 per cent. of magnesium oxide. When dolomitic limestones are employed, the reason is, in general, to introduce magnesia into the batch in order to modify the properties of the glass. Insoluble matter denotes the presence of foreign minerals, frequently sand, and the iron content of the insoluble portion should be determined. A general discussion of limits of impurities is given below. Since limestone dissolves in fused soda-ash or saltcake it need not be crushed exceptionally finely before adding to the batch, but pieces larger than 0.25 inch should not be used.

The following are some typical analyses of calcium compounds.

TABLE XXVIII—COMPOSITION OF CALCIUM COMPOUNDS.

	<i>Limespars.</i>		<i>Limestones.</i>				<i>Slaked Lime.</i>
	1	2	1	2	3	4	
			Wirksworth.	Buxton I.	Buxton II.	Threshy	
CaO	52.78	55.33	54.93	54.80	52.18	50.24	71.51
MgO	0.20	0.62	0.24	0.11	0.74	1.58	0.78
Al_2O_3	0.03	0.17	0.10	0.69	0.32	1.82	1.26
SiO_2	—	0.47	—	—	4.15	—	—
Insoluble ..	5.04	0.63	1.77	1.78	5.8	2.34	2.64
Total Fe_2O_3 ..	0.03	0.11	0.75	0.16	0.68	0.70	0.61
Loss on ignition ..	41.62	43.15	42.58	42.88	40.62	41.64	23.62

Quick Lime (Burnt Lime). (*Calcium Oxide. Formula, CaO . Molecular weight, 56*).—Calcium carbonate decomposes on strongly heating into quicklime and carbon dioxide gas; on the other hand, if a current of carbon dioxide is passed over quicklime, calcium carbonate is again formed. The decomposition of calcium carbonate is thus a reversible action, and may be represented by the equation:

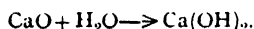


If the carbonate is heated in a closed vessel a fixed pressure is attained which is called the *dissociation pressure* for that temperature. At this point the gas and the quicklime will recombine at the same rate as the calcium carbonate decomposes and a state of equilibrium will result. For each temperature there is a definite dissociation pressure, the value of the latter increasing with temperature increase. When the carbonate is heated in an open vessel, there will be no general decomposition until the dissociation pressure is equal to atmospheric pressure, at which point the liberated carbon dioxide gas can freely pass away. The temperature at which the dissociation pressure is equal to the normal atmospheric pressure is about 840°C. , and consequently for calcining limestone this temperature at least must be reached, the usual temperature of lime kilns being 900°C. and above. The old method of lime burning was to

lay the limestone in layers between layers of fuel. The modern method, which not only is more expeditious, since it is a continuous method, but also yields a purer product, consists in passing the limestone down shaft kilns heated by producer gas.

Quicklime readily absorbs moisture, giving slaked lime, and if kept over a long period is best preserved by heaping in a powdered condition.

Slaked Lime. Calcium Hydrate. (*Formula, Ca(OH)_2 . Molecular weight, 74*).—On "slaking" burnt lime the following reaction occurs:



Slaked lime is more constant in composition than quicklime. It absorbs carbon dioxide, however, to give calcium carbonate again, and consequently its composition should be periodically checked.

(91) **The Relative Advantages of Limestone, Quicklime, and Slaked Lime.**—Since calcium carbonate is the calcium compound found in nature, it is obvious that this will be relatively the cheapest material to use in the glass batch. Further advantages of this substance are that the carbon dioxide which is evolved is a useful agent in fining the glass, and it also acts as a diluent of the acid gases produced when saltcake is one of the batch constituents. The calcining of limestone adds to its cost and may add to the impurities present in it. On the other hand, organic impurities are burnt out in the process, so that the quicklime, particularly when made by the modern kiln method, may be somewhat purer than the limestone from which it was prepared. The great drawback in the use of quicklime is the rapidity with which its composition varies with exposure, making correct batch preparation a matter of extreme difficulty. The same fault may be found, though in a much less degree, with slaked lime, which is preferable to quicklime from the point of view of stability of composition. In America much of the limestone is burnt before use, but the tendency is now towards the use of the unburnt material. Quicklime and slaked lime are powdered, or easily obtained in this state, whilst limestone requires crushing, but the process is not very expensive, since the size of the ground material need not be very small. Less important still is the fact that limestone requires extra heat for its decomposition in the furnaces, for the extra heat has already been used in the case of quick or slaked lime in the calcining process. Little is known as to the differences which may occur in the process of glass-making when quicklime, slaked lime, or limestone are used. Hodkin and Turner* have noted that in the cases of soft and very soft soda-lime glasses (the former such as used for bottles, etc.), batches comprised of sand, soda-ash, and quicklime are the quickest melting, and at corresponding temperatures are the most fluid, the rate of melting of a sand-soda ash-limestone batch being less than that of the sand-soda ash-slaked lime. With saltcake as a source of alkali the batches containing sand, saltcake and limespar melt quicker than those of sand, saltcake and burnt lime, the latter giving the most viscous of all the batches, whilst the slowest melting is the sand-saltcake-burnt lime batch. With batches for glass of a harder type, such as is used for

* *J. Soc. Glass Tech.*, 1921, 4, 188.

window glass (*i.e.*, with lower alkali and higher lime contents), the slaked lime batch melts quickest. When soda-ash is the source of alkali, the limespar batch is slowest in melting, whilst with saltcake little difference in the rate of melting is found.

Limes which are a by-product of the chemical and soap industries are now used to some extent for glass manufacture. Their compositions are widely variable, as the following analyses will show:

TABLE XXIX — BY-PRODUCT LIME.

	Soap Works Lime.		Chemical Lime.
	1	2	
CaO	45.6	54.30	54.0
MgO	0.6	0.54	0.15
Al ₂ O ₃	2.6	0.80 (sol.)	1.37
SiO ₂	2.0	0.37	3.00
Insoluble ..	—	—	—
Total Fe ₂ O ₃ ..	0.3	0.10	0.32
Loss on ignition ..	49.1	42.53	40.68

(92) **Standards of Purity of Lime Compounds.**—The American Bureau of Standards has recently laid down a specification for limestone, quicklime, and slaked lime for use in the manufacture of glass.* It states that quicklime should not contain more than 3 per cent. of carbon dioxide, slaked lime not more than 5 per cent., and the latter should contain enough water to have slaked all the quicklime originally present. Three grades of the above materials were arranged with limits as specified in Table XXX.

TABLE XXX.—THE PERCENTAGE COMPOSITION OF THE NON-VOLATILE PORTION OF LIMESTONE, QUICKLIME OR SLAKED LIME.

Ingredients.	Class I.		Class II.		Class III.	
	(Maxi- mum.)	(Mini- mum.)	(Maxi- mum.)	(Mini- mum.)	(Maxi- mum.)	(Mini- mum.)
CaO + MgO ..	—	96	—	91	—	83
Fe ₂ O ₃	0.2	—	0.4	—	0.8	—
SO ₃ + P ₂ O ₅ ..	1.0	—	1.0	—	1.0	—
SiO ₂	4.0	—	9.0	—	17.0	—
Al ₂ O ₃	3.0	—	5.0	—	5.0	—

The percentage composition of the non-volatile portion of limespar 1 (Table XXVIII.) is CaO + MgO = 98.4, Fe₂O₃ 0.20, SiO₂ 0.83, Al₂O₃ 0.30,

* Circular No. 118, Bureau of Standards, December 8, 1921

and it would come under category I. Limestone 3 (Buxton II.) would have the non-volatile composition $\text{CaO} + \text{MgO} = 89.1$, Fe_2O_3 1.15, SiO_2 7.0, and thus because of its iron oxide content would fall outside the third class. A simple classification based on the iron oxide content would be the following:

<i>Fe₂O₃ Content per Cent.</i>				
For white bottles	up to 0.10
Pale green bottles	0.10 to 0.30
Dark green bottles	above 0.30

(93) **The Effect of Lime on Glass.**—The use of lime in glass is important, since the calcium silicate produced gives great chemical stability to the resulting substance. It must not be forgotten that lime is a powerful flux, reacting with silica at comparatively low temperatures. Quite large amounts of calcium oxide can be incorporated in glass, and samples of soda-lime glass have been produced at the Department of Glass Technology, University of Sheffield, which contain 40 per cent. of lime, the glass melting extremely rapidly and having a very low viscosity when hot. When the lime content is high, however, there is a tendency for the separation of calcium meta-silicate (Wollastonite) as "dog."

The viscosity range of glasses rich in lime is short, and although such glasses are more fluid at higher temperatures than high soda glasses, they rapidly stiffen on chilling. For this reason they are useful for hand working, or for slower semi-automatic machines where, on being blown, the article is required to set fairly quickly.

The danger in the use of high lime glasses for rapid machine manufacture is that parts may rapidly chill and refuse to blow into shape, this applying particularly to the necks of bottles. Again, increase of lime increases the heat conductivity of the glass and raises the annealing temperature, rendering it necessary to place the articles rapidly in the lehr after blowing. Beneficial effects of the addition of calcium oxide are that the rate of expansion is lowered, and the mechanical strength increased, all tending towards good thermal endurance whilst the resistance to atmospheric weathering and to the attack of reagents is largely increased. The following table gives examples of the use of lime in gears.

TABLE XXXI.—BATCHES FOR LIME-CONTAINING GLASSES.

(The amounts of decolourisers given below need adjusting to the purity of the materials used. For further information on this point see "Decolourisers.")

<i>Hand-made Bottles.</i>						
					1	2
Sand	1,000	1,000
Soda-ash	300	300
Salt lake	100	—
Limestone	500	457
Arsenious oxide	—	7

Machine-made Bottles.

	O'Neill's Machine and Similar Types.	Owen's Machine.
Sand	1,000	1,000
Soda-ash .. .	375	375
Limespar .. .	170	175
Borax .. .	1	—
Arsenious oxide .. .	1	—
Powder blue .. .	0.06	—
Selenium .. .	0.03	—

Window Glass.

	1	2	3	4
Sand	1,000	1,000	1,000	1,000
Soda-ash .. .	260	—	310	250
Saltcake .. .	60	420	65	75
Limestone .. .	370	300	320	350
Powdered anthracite .. .	—	17.5	3	4

Cheap Pressed Ware.

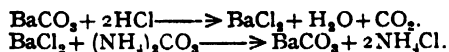
Sand	1,000
Soda-ash .. .	400
Limespar .. .	180
Arsenious oxide .. .	1
Selenium .. .	0.03

Table Ware.

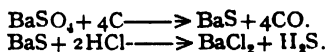
	1	2	3
Sand	1,000	1,000	1,000
Potash (80-85 per cent.) .. .	340	130	220
Soda-ash .. .	—	150	150
Limespar .. .	170	120	160
Zinc white .. .	—	—	60

Bohemian Crystal.

(94) **Barium Oxide.** (*Formula, BaO. Molecular weight, 153.*)—Barium oxide has the greatest molecular weight of any of the common oxides used for glass-making except that of lead. It is not found in nature in the free state, but chiefly in the form of *witherite*—barium carbonate, BaCO_3 , and *barytes* or *heavy spar*—barium sulphate, BaSO_4 , the latter being the more abundant. In glass manufacture barium carbonate is the compound most used, and natural crystalline witherite of good quality is its best source. Impure varieties are improved by dissolving in acid, filtering off impurities, and reprecipitating with sodium or ammonium carbonate:



A further source of the carbonate is heavy spar, which is first heated with carbon to reduce it to the sulphide, the latter then being dissolved in acid. From the resultant solution the carbonate is precipitated as before:



The carbonate may be added to the batch as is limestone, being decomposed in precisely the same way during the founding of the glass.

In place of barium carbonate, the sulphate may be used, but it must be accompanied by a reducing agent, which, as in the case of saltcake, is best supplied in the form of coke or coal. The quantity of carbon needed is, according to Fettke, 4 to 7 per cent. of the barium sulphate used.

The chief impurities in witherite are silica, lime, magnesia, alumina, and iron oxide, the most objectionable, again, being iron oxide. A good sample should dissolve practically completely in acid and show a low iron content. Another impurity sometimes found is cobalt oxide, since barium compounds are largely used in filling paper, in which case a small amount of cobalt blue powder is added to produce a good white colour.

(95) **The Properties of Barium-containing Glasses.**—Barium oxide acts in a similar manner to calcium oxide in the glass, decreasing the solubility, though not to such a great extent as lime, and causing increased brilliancy and strength. Barium carbonate is not so easily decomposed by heat as calcium carbonate, but barium silicate is more readily fusible than calcium silicate. The density and index of refraction of barium glasses are higher than those of the corresponding lime glasses, but not so great as those of lead glasses. In hardness and coefficient of expansion they do not vary much from lime glasses, but they have a lower specific heat. Barium glasses have a higher elasticity and toughness than lime glasses.

Comparing barium glass with lead glass, the former is more fluid at high temperatures, but sets more quickly on cooling, that is, it possesses a shorter viscosity range. For this reason it is particularly suitable for pressed glassware (see Table XXXII.). Since barium compounds are not reduced by furnace gases, barium glasses may be melted in open pots, whilst they work almost as well as lead glasses, are only slightly harder, and when struck possess a good ring. They are not suitable for "acid polishing"—that is, the production of a brilliant surface by treatment with strong hydrofluoric acid.

Barium glasses are largely employed for optical purposes, but, according to Peddle,* simple alkali-barium oxide-silica glasses are not stable enough for optical glass, being badly weathered on exposure, so that other constituents must be added to give the requisite stability. Glasses of high barium content also tend to devitrify. Williams and Cox† obtained barium-potassium-zinc glasses which appeared to have a higher lustre than high quality cut glass, whilst the hardest type of sodium-barium glasses (those low in soda) had a melting-point as high as 1550° C. As in the case of lead glasses, barium glasses have a strong corrosive action on the pots.

TABLE XXXII.—BATCHES FOR PRESSED WARE.

	1	2	3
Sand	1,000	1,000	1,000
Potash	100	166	50
Soda-ash	250	144	300
Barium carbonate	250	110	100
Nitre	60	—	50
Limespar	50	44	100
Manganese dioxide	—	—	2

(96) **Lead Oxide.** (*Formula, PbO. Molecular Weight, 223*).—Lead is chiefly added in the form of red lead—though sometimes litharge, which corresponds to the state of oxidation of the lead in the glass, is employed.

Litharge. *Formula, PbO.*—Yellow oxide of lead or litharge is obtained by heating the metal until it is oxidised, on movable open hearths in cupellation furnaces. Litharge melts at 880°C .

(97) **Red Lead. Minium.** (*Formula, Pb₃O₄. Molecular weight, 685*).—Prolonged heating of litharge at not above 450°C . in presence of air produces red lead—the action being reversed with too high a temperature:



Pure red lead corresponds to 97.67 per cent. of its weight of litharge, but in practice the reaction is never complete, the red lead always containing more or less litharge, and its colour varying from yellow to bright scarlet according to the proportion of red lead actually present. As an example of the composition, a commercial red lead of good quality was found to contain 98.2 per cent. of PbO, corresponding to a red lead content of 78 per cent. and a litharge content of 22 per cent.

The impurities likely to be present in lead oxides are insoluble matter from the furnaces (silica, etc.), iron from the tools, copper, tin, lead sulphate, barium sulphate, and unoxidised lead. Copper would colour the glass blue, whilst metallic lead would give a black or mirror-like appearance to the glass. Since lead oxide is only used for the more expensive glasses it is desirable to obtain the material in a pure form.

(98) **Relative Advantages of Red Lead and Litharge.**—Litharge, if pure enough, is quite suitable for glass-making, and is, of course, cheaper than red lead. On the other hand, the excess of oxygen which red lead contains is given off at a comparatively low temperature in the furnace, the decomposition taking place readily above 550°C . Since the great difficulty with lead glasses is the tendency to reduction, the presence of oxidising conditions, such as the decomposition of the red lead tends to create, helps in the process of melting. It will be seen that the oxygen is given off before melting really begins, hence the gas has no influence on the fining of the metal. A more important advantage of red lead is that litharge often contains unoxidised lead particles, which have escaped attack through being coated with oxide, whilst the subsequent prolonged oxidation to form red lead generally converts all the free metal to oxide. The variability of the composition of red lead renders the analysis of each successive consignment a necessity.

(99) **The Properties of Lead-containing Glasses.**—Lead oxide largely increases the density and refractive index of glass, giving types suitable for optical glass and table ware. "Strass," used for the manufacture of artificial gems, is a glass of high lead content and of great brilliancy. Lead glass is softer than lime glass and can be cut and polished more readily, hence it is largely used for cut glass ware. The greatest brilliance in effect is obtained when lead oxide is used in conjunction with potash as the alkaline oxide. Many colouring agents give better effects in lead glass than in lime glass. The type of lead glass used for the best table and cut glass ware is "full crystal" or "English crystal" which contains about 33 per cent. PbO, 54 per cent. SiO₂, and 13 per cent. K₂O. "Semi-

crystal" which contains 17 to 30 per cent. PbO , and in which the potash is wholly or partly replaced by soda, whilst other basic oxides such as lime or baryta are introduced, is employed for cheaper glassware, such as coloured glass, electric lamp bulbs, etc. Peddle* considers that the best lead glass as regards colour, density, brightness, durability, melting and working, for high-grade cut glass ware would be of the composition SiO_2 42 per cent., PbO 48 per cent., Na_2O 3 per cent., K_2O 7 per cent. A large proportion of optical glasses are lead-containing glasses—the oxide finding extensive employment in this direction. According to Peddle,* where the corresponding oxides are employed weight for weight, lead glasses are more soluble, and do not resist weathering action so well as lime glasses. Distinctly greater stability is imparted, so Hodkin and Turner† have shown, by the addition of a small amount of boric oxide to lead glasses. Glass high in lead is particularly susceptible to attack by moist atmospheres containing acid fumes (particularly sulphuretted hydrogen), which produce iridescence on the surface of the glass. Attack on pots and refractories is much more severe in the case of lead than with lime glasses.

Free lead oxide is reduced to the metal by hydrogen at 235°C. , and in the manufacture of lead glass the tendency to reduction and deposition of lead may cause some difficulty. Until recently closed pots only were used for the melting operation. It is now recognised that open pots may be successfully employed if the right conditions are obtained. Factors to be watched are, the prevention of reducing materials in the batch (this includes batch materials or extraneous impurities), the addition of oxidising agents such as nitre, the production of an oxidising atmosphere as possible in the furnace, and the carrying out of the melting at a high temperature in order to reduce the time occupied, hence the chances of reduction. The first condition prevents the use of saltcake or barium sulphate, which need carbon to reduce them, and of selenium and sulphur for decolourising or colouring, since these are reducing agents.

TABLE XXXIII.—BATCHES FOR LEAD GLASSES.

Crystal Glass for Table Ware (English Crystal).

	1	2	3	4
Sand	1,000	1,000	1,000	1,000
Potash	400	330	300	260
Red Lead	800	660	680	700
Potassium nitrate		40	50	35
Borax		30	—	40
Arsenious oxide		2.5	—	—
Manganese dioxide		2.0	2.0	2.0

Semi-Crystal Glass.

	1	2
Sand	1,000	1,000
Potash	350	280
Limespar	140	130
Barium carbonate	—	130
Red lead	100	260
Potassium nitrate	—	30
Nickel oxide ..	0.02	—

* *J. Soc. Glass Tech.*, 1921, 5, 72.† *Ibid.*, 1920, 4, 125.

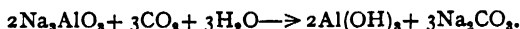
Electric Light Bulbs.

	1		2
Sand	1,000	Sand	1,000
Soda-ash	330	Soda-ash	140
Red lead	480	Potash	200
Borax	90	Red lead	160
Felspar	70	Limespar	120
Sodium nitrate	50	Manganese dioxide	0.5
Manganese dioxide	2	Nickel oxide	0.02

(100) **Aluminium Oxide.** (*Formula, Al_2O_3 . Molecular weight, 102.*)—The chief sources of aluminium oxide (or alumina) for glass-making are the oxide itself, the hydroxide, or the mineral products *kaolin*, *felspar*, etc.

Aluminium Oxide. *Calcined Alumina, Al_2O_3 . Molecular weight, 102.*—Alumina occurs naturally as *corundum*, *ruby*, *sapphire*, and *emery*. The natural sources of the pure mineral are small, and the artificial variety, obtained from other aluminium compounds by precipitation of the hydroxide and subsequent ignition is invariably preferred.

Aluminium Hydroxide. *Hydrated Alumina, $Al(OH)_3$. Molecular weight, 78.*—The mineral *bauxite* is a hydrated oxide of aluminium having the formula $Al_2O_3 \cdot 2H_2O$. It is contaminated largely with iron oxide and is purified in the following manner: The mineral is fused with sodium carbonate to produce sodium aluminate Na_3AlO_3 , and this is extracted by lixiviation with water, in which it is soluble, from the insoluble iron hydroxide simultaneously produced. The sodium aluminate itself is commercially available and could be used whenever the accompanying sodium oxide did not render the material undesirable. In practice the aluminate is usually decomposed in solution by a stream of carbon dioxide gas, with the consequent precipitation of aluminium hydroxide:



The product is fairly pure but rather costly. The moisture content is also variable, and ignition to the oxide is desirable.

Kaolin. *China Clay. (Formula, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. Molecular weight, 258.)*—Kaolin is a decomposition derivative of felspathic rocks, and is prepared for the manufacture of pottery on a large scale. Supplies of the material are obtained from Cornwall and Devon in England, Eisenburger and Engelmansreuther in Germany, Arkansas, Alabama, and Colorado in the United States.

The product often deviates in composition from pure kaolin, which contains 40 per cent. Al_2O_3 , 46 per cent. SiO_2 , and 14 per cent. water, the state of purity depending on the size of the particles and the extent to which it is washed. Impurities are chiefly quartz, felspars, micas, lime, magnesia, and iron oxide, the last of which is again the most deleterious. Kaolin heated above $600^\circ C$. loses its combined water.

Felspars are, with the exception of silica, the largest components of igneous rocks. They comprise:

Potash felspar (microcline or orthoclase), $K_2O, Al_2O_3, 6SiO_2$, containing 16.9 per cent. K_2O , 18.4 per cent. Al_2O_3 , and 64.7 per cent. SiO_2 .

Plagioclase felspars, including (a) *soda felspar (albite) $Na_2O, Al_2O_3, 6SiO_2$* , containing 11.8 per cent. Na_2O , 19.6 per cent. Al_2O_3 , 68.6 per cent.

SiO_2 , and (b) *lime felspar (anorthite)* $\text{CaO}, \text{Al}_2\text{O}_3, 2\text{SiO}_2$, containing 20.1 per cent. CaO , 36.6 per cent. Al_2O_3 , 43.6 per cent. SiO_2 . Albite and anorthite are found together in varying proportions in nature.

Many felspar deposits are known, the products of which correspond, more or less, to the compositions given above, variations being due to the presence of impurities, and to a mixture of the different felspar types. The most constant in composition are the potash felspars, and it is these which are chiefly used. Sources of potash felspar are Tresayes in Cornwall, and Norway, Germany, North America, etc.

Igneous rocks are used to some extent on the Continent, but, in general, their composition is very variable and their impurities great.

Nepheline, $\text{Na}_2\text{O}, \text{Al}_2\text{O}_3, 2\text{SiO}_2$, is a desirable substance from the glass-making point of view, and the igneous rock, *phonolith*, which contains it, is often used in Germany as a batch constituent.

Aluminous Sand.—Sand containing a considerable amount of kaolin and of felspar has often been used for glass in which a high alumina content has been desired. A particular instance is the use of Martinsroda sand, containing about 3.6 per cent. of alumina, for Thuringian thermometer glass.

(101) **A Comparison of Alumina-bearing Materials.**—In the manufacture of optical glass purity is desired, and in this case it is best to use alumina, calcined or hydrated. For glassware in which purity is of less importance, kaolin or felspar can be added, unless a suitable alumina-bearing sand is available. Singer found that whether calcined or hydrated alumina was used it rendered the melts easier to fuse in the same degree, whilst Springer also found no difference in effect between kaolin and hydrated alumina. With a soft-melting glass, however, there is a tendency for the kaolin, during its composition, to be driven to the surface and there form a scum.

TABLE XXXIV.—THE COMPOSITION OF ALUMINA-BEARING SUBSTANCES

	SiO_2 .	Fe_2O_3 .	TiO_2 .	Al_2O_3 .	CaO .	MgO .	K_2O .	Na_2O .	Loss on Ignition.
Hirschau kaolin ..	48.05	0.41	—	37.41	—	—	2.58	2.58	11.53
Norwegian felspar	64.44	0.65	—	18.75	0.27	—	13.82	2.40	—
Tresayes felspar ..	64.21	0.18	—	19.66	0.35	0.07	12.35	2.79	0.73
Zittau phonolith ..	59.17	3.39	—	19.74	0.92	0.15	4.56	8.88	1.18
Martinsroda sand	61.38	0.47	—	3.66	0.31	—	3.49	3.49	—
Spital sand ..	94.60	0.06	—	2.99	0.20	0.14	1.44	—	0.65
Meldon crushed rock ..	71.07	0.27	0.06	16.79	0.7	0.05	3.83	4.92	1.87

(102) **The Properties of Alumina-containing Glasses.**—Opinions in regard to the value of alumina in glass vary greatly, and in few points are the various observers in agreement. The fact that the oxide prevents devitrification in glass in which it occurs, however, is not disputed. In regard to melting Pelouze,* Springer,† and Frink‡ claim that alumina

* *Ann. Chim. Phys.*, 1867, (4), 10, 184; *Compt. rend.*, 1869, 64, 53.

† *Ker. Rundschau*, 1915, 23, 272

‡ *Trans. Amer. Cer. Soc.*, 1909 11, 99

renders melting more difficult, but a large body of opinion, including that of Appert* and Singer† inclines to the opposite view. In a series of tests, Dumbleby, Hodkin, and Turner‡ found that a moderately hard soda-lime glass was more readily fusible by the addition of small amounts of alumina, and that a glass of the percentage composition SiO_2 , 74.13; Al_2O_3 , 2.67; CaO , 9.74; Na_2O , 13.54; melted and fined more easily than the corresponding lime glass without alumina.

That the viscosity of the glass is greater when the alumina in it exceeds 3 per cent. is a view held by Frink. Turner and his co-workers also noted the greater viscosity of alumina-lime glasses as compared with lime glasses.

According to Frink, homogeneity of the glass from tank furnaces is improved by the presence of 3 per cent. of alumina, an opinion at variance with that of Henrivaux.§ Appert claims that the presence of alumina allows replacement of a portion of the alkali by lime, giving a harder, more durable, and more elastic glass.

Frink|| states that alumina has the tendency to increase surface tension of the metal when suddenly chilled, causing the formation of a tenacious skin which does not take on the imperfections of any mould surface against which it is pressed or blown. The reduction of the coefficient of expansion and the increase of tensile strength of the glass are also stated to be points in its favour, as are the increase of hardness and brilliancy.

Only Henrivaux¶ claims that alumina-containing glass is more difficult to anneal than lime glass. English and Turner** have recently shown that the annealing temperature of alumina-containing glasses is generally less than that of the corresponding lime glasses, no case being found in which it is greater.

Durability of the glass is increased, as is its resistance to acids by the addition of alumina, whilst lamp-working properties are improved. On the whole, we may say that for bottle and similar glass addition of some alumina is a distinct advantage.

It is not usual to employ large quantities of alumina in glasses, but certain Continental bottle glasses contain as much as 15 per cent. of this oxide.

(103) **Zinc Oxide.** (*Formula, ZnO . Molecular weight, 81.*)—Zinc oxide itself, known generally as "zinc white," is usually used in the batch. The pure material dissolves completely in acid without liberation of bubbles of carbon dioxide, and it should contain no lead, copper, or iron as impurities.

Zinc carbonate may also be employed, but it has a variable zinc oxide content, and the natural variety also contains silica.

The use of zinc oxide is limited to certain special glasses. In glass, the coefficient of thermal expansion of zinc oxide is one of the lowest of those of the basic oxides, and this, coupled with the high stability of the glasses under strain, renders them good for use for materials which

* *Compt. rend.*, 1896, **122**, 672.

† *Ker. Rundschau*, 1917, **25**, 142.

‡ *J. Soc. Glass Tech.*, 1921, **5**, 107.

§ *J. Pharm. Chim.*, 1889, (5), **19**, 446.

|| *Trans. Amer. Cer. Soc.*, 1909, **11** 99

¶ *Loc. cit.*

** *J. Soc. Glass Tech.*, 1921, **5**, 115.

undergo sudden temperature changes. The chemical stability of zinc-containing glasses fits them for use in the form of laboratory ware. Glasses containing zinc oxide have a refractive index lying between that of lime-containing and of barium oxide-containing glasses of similar composition, so that "zinc crowns" are important from an optical standpoint. Zinc oxide is also employed to a small extent in pressed and opal glasses.

Fusibility is decreased by the presence of zinc oxide in the batch, so that good melting conditions are required—namely, a hot furnace and pot. In practice the proportion of zinc oxide used seldom exceeds 50 parts per 1,000 of sand, whilst 80 parts per 1,000 would give a glass regarded as being rich in zinc oxide.

(104) **Magnesium Oxide.** (*Formula, MgO. Molecular weight, 40.*)—Magnesium carbonate occurs fairly widely spread in nature as magnesite, $MgCO_3$, or, as we have pointed out in discussing limestone, as the double carbonate dolomite, $MgCO_3 \cdot CaCO_3$. Smaller sources of the oxide are the sulphate, as Epsom salts, $MgSO_4 \cdot 7H_2O$, and *kieserite*, $MgSO_4 \cdot H_2O$, and the chloride as *carnallite* and *kainite*. Natural silicates containing magnesium are *olivine*, Mg_2SiO_4 , *enstatite*, $MgSiO_3$, and *asbestos*, *serpentine*, *talc*, etc.

From the point of view of the glass manufacturer magnesite, dolomite, or the oxide obtained from these by calcination, only are suitable, and may alone be considered.

TABLE XXXV.—COMPOSITION OF MAGNESITES AND DOLOMITES.

Constituents.	Magnesites.			Dolomites.		
	Grecian.	Washington (U.S.A.).	Canadian.	Warm- sworth.	Raisle (California).	Gerolstein (Germany)
				1 2		
CaO	1 to 2	0.5 to 2	4 to 10	32.10 30.48	30.60	29.64
MgO	44 „ 66	45 „ 46	34 „ 40	21.79 20.00	21.52	21.11
Al ₂ O ₃	0.2 „ 1	1 „ 2	0.2 „ 1	0.80 0.11	0.28	0.22
Fe ₂ O ₃	0.1 „ 0.5	—	—	0.21 1.51	Trace	0.80
FeO	—	0.2 „ 1	0.2 „ 1	—	—	—
Loss on ignition	49 „ 52	49 „ 51	49 „ 51	44.80 44.46	47.70	46.51
Non-volatile in- soluble ..	0.5 „ 2	0.5 „ 4	1 „ 2.5	0.23 1.88	0.23	1.23

Purest magnesites are found in Greece, India, South Africa, and America, and these are available in fairly large amounts, although at a price materially greater than that of limestone. Great Britain possesses no magnesite deposits, but several dolomites are available. Unfortunately, they almost all possess an iron oxide content appreciably above the limits for best glass. The purest variety is found in South Yorkshire around Conisborough and Warmsworth, but average samples seldom have a ferric oxide content less than 0.5 per cent.

Because of the contamination with iron oxide, dolomite has found little use hitherto in colourless glass made in this country, but in America, where purer dolomite is obtainable, it has extensive use for colourless glass bottles, electric lamp bulbs, etc.

On p. 108 is given the composition of some typical magnesites and dolomites.

(105) **Properties of Magnesia-containing Glasses.**—Up to the present magnesia has been used but little in glass manufacture, and even when used, in the form of dolomitic limestone, has probably been employed without a true appreciation of its action or possibly even of its presence.

Dolomite has been employed hitherto, mainly for the manufacture of bottle glass. Non-lead glass, for electric lamp bulbs, in which the lead oxide is substituted by magnesia, has more recently been made.

Not much systematic work has been published on the properties of magnesia-containing glass, the only research of any importance having emanated from the Department of Glass Technology, Sheffield University. Davidson, Hodkin and Turner* examined a series of soda-magnesia trisilicate glasses ranging from $6\text{SiO}_2, 2\text{Na}_2\text{O}$ to $6\text{SiO}_2, 0.9\text{Na}_2\text{O}, 1.1\text{MgO}$, and it was found that small amounts of magnesia tend to give glasses having a rapid melting rate. In large quantities, however, it gives a glass not easy to melt, whilst the viscosity of high magnesia glasses is great—much greater than that of corresponding lime glasses, and they show a tendency to stringiness and cordiness not shown with those containing lime.

When magnesia replaces lime molecularly in a soda-lime glass† at first readier melting and easier working ensue. Thus a glass containing 9.26 per cent. of calcium oxide will have a slower rate of melting and be more difficult to work than the glass with 6.43 per cent. of calcium oxide and 2.58 per cent. of magnesia (or any intermediate glass also). Beyond this point, however, further addition of magnesia becomes decreasingly beneficial, and when the two oxides are together in equi-molecular proportions—as is the case when the limestone used is entirely a dolomitic one—it is not so easy to melt as the lime glass and somewhat less easy to work. Magnesia improves the lamp-working properties of lime containing glass and diminishes the tendency to devitrification. English and Turner‡ have shown that magnesia, as compared with lime, tends to give a lower annealing point to the glass of which it is a component.

A glass which should be useful from the point of view of quick melting, resistance to devitrification, and low annealing temperature would be that having the molecular composition $6\text{SiO}_2, 1.2\text{Na}_2\text{O}, 0.6\text{CaO}, 0.2\text{MgO}$, corresponding to the approximate percentage composition SiO_2 75, Na_2O 15, CaO 7, MgO 2. It would be obtained from either of the batches given below:

	1	2
Sand	1,000	1,000
Soda-ash	350	350
Limestone	168	154
Magnesite	12	—
Dolomite	—	26

* *J. Soc. Glass Tech.*, 1919, 3, 275.

† *Ibid.*, 1921, 5, 353.

‡ *Ibid.*, 1919, 3, 278; 1921, 5, 357.

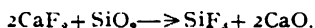
CHAPTER IX

THE RAW MATERIALS USED IN GLASS MANUFACTURE— *Continued*

(C) *Miscellaneous Materials.*

(106) **Fluxes.**—In melting the batch some of the substances composing it are found to be valuable for the rapid chemical activity which they induce, causing the batch to melt together and form glass. We have mentioned in this category the sodium and potassium compounds, lime, boric oxide, and borax. In general it is found that fluxing materials also provide either one or more of the oxides comprising the glass, as in the cases of the ones alluded to, or have some other function in glass manufacture besides that of a flux. Examples of this are sodium and potassium nitrates, which are also oxidising agents, and probably *arsenic* and antimony oxides under certain conditions.

Calcium Fluoride. Fluorspar. (*Formula, CaF_2 . Molecular weight, 78.*)—Calcium fluoride or fluorspar is mostly employed in conjunction with felspar as an opaliser. It is used occasionally, however, as a flux. In the glass batch it reacts with silica to give the gas, silicon fluoride SiF_4 :



The result of the action is to diminish the silica content of the batch and to increase the lime. Calcium fluoride attacks the refractories badly, whilst the liberated silicon fluoride attacks the brickwork of the flues.

When fluorspar is used some of the fluorine is not expelled, and its presence in the glass gives a product with low refraction and dispersion, rendering it valuable for optical purposes.

Other Fluxes.—Where it is required to obtain a batch of maximum fluxibility containing a fixed amount of alkali, the introduction of sodium or potassium nitrate—in place of some of the sulphate or carbonate—is found to be of distinct advantage.

(107) **Oxidising Agents.**—A number of substances capable of liberating oxygen are employed in glass manufacture. They include sodium and potassium nitrates, red lead, manganese dioxide, and less commonly, barium peroxide. Oxygen so produced may serve several purposes. It may be employed to combine with, and so decompose, any organic matter in the batch, thus preventing discolouration of the glass. It may also prevent reduction of easily reducible substances, when such reduction would give harmful results. What is meant by the term “reduction”

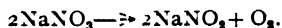
may best be expressed by "loss of oxygen." For instance, litharge (lead oxide) is most easily decomposed into metallic lead and oxygen, the oxygen being removed by agents, such as carbon or carbon-containing compounds, in the furnace gases.

By supplying an oxidising agent to a batch containing litharge the tendency to reduction is minimised. Again, it is frequently desirable to maintain the iron present in a glass in the less highly coloured ferric condition (see Iron Compounds), and the reducing tendency of the furnace gases can be counteracted by the presence of an oxidising agent. In the above cases the most usual agents employed are the nitrates of sodium and potassium. "Fining," an action shortly to be described, is sometimes assisted by the gas liberated from oxidising agents, but since these in general are practically completely decomposed before founding is complete, their influence in fining is not very great. We may now consider in detail the various oxidising agents employed.

Sodium Nitrate. *Soda Nitre. Chile Saltpetre.* (Formula, NaNO_3 . Molecular weight, 85.)—The Tarapaca plateau, along the west coast of South America, is the source of most of the sodium nitrate at present used. Deposits are there found which are the decomposition products of organic matter in the presence of calcium carbonate and sodium chloride. They consist of layers of material of varying composition and nitrate content. Extraction is performed by water in a series of tanks heated by steam, after which the nitrate solution is decanted off, cooled, and the salt so crystallised out. Thorpe gives the following compositions for the crystallised salt:

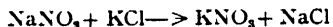
						Quality	
						1st.	2nd
NaNO_3	96.5	95.2
NaCl	0.75	2.5
Na_2SO_4	0.45	0.6
H_2O	2.3	1.7

Of the impurities, neither sodium chloride nor the sulphate is particularly harmful, whilst iron compounds are generally small in amount. Sodium nitrate fuses at 316°C . and decomposes at higher temperatures, yielding, at first, sodium nitrate and oxygen:



On further heating sodium oxide, oxygen, nitrogen, and nitrous oxide (N_2O) are all obtained. Sodium nitrate is very hygroscopic, and for this reason is generally replaced by the potassium salt, which less readily absorbs moisture.

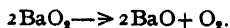
Potassium Nitrate. *Nitre.* (Formula, KNO_3 . Molecular weight, 101).—On mixing and heating solutions of sodium nitrate and potassium chloride, the following reaction takes place:



The bulk of the sodium chloride is at once precipitated, being much less soluble than any of the other reagents present, and it is removed. Partial concentration serves to precipitate still more of the sodium chloride, which is filtered off. Further concentration now brings down

potassium nitrate in a fairly pure form, the salt being purified by dissolving in fresh water and recrystallising. Impurities found in nitre are, in general, much the same as those in sodium nitrate. Potassium nitrate melts at 339°C. , and at higher temperatures breaks up in a similar way to sodium nitrate, although its oxygen is not given off at so low a temperature.

Barium Peroxide. (*Formula, BaO_2 . Molecular Weight, 169.*)—Shortage of nitrates in time of war compelled German manufacturers to seek other oxidising agents, and barium peroxide was the most favoured. Oxygen is liberated from it at 700 to 800°C. according to the reaction:



Springer found a so-called "nitre substitute" to consist of 77.3 per cent. BaO_2 , 13.9 per cent. BaCO_3 , and 6.2 per cent. BaO . At least four times as much barium peroxide as nitre is needed to produce the same amount of oxygen, and such a quantity introduces an appreciable amount of the base, barium oxide, into the glass.

Pyrolusite. *Manganese Dioxide, MnO_2 ,* is chiefly important for its colouring action, and will be described with other colouring agents. It is, however, an oxidising agent, although this function is not very important.

(108) **Fining Agents.**—As the melting of a glass batch proceeds large numbers of exceedingly small bubbles of gas, the so-called "seed," remain enmeshed in the metal, the viscosity of which only allows them to escape when fairly large in size. Increase of temperature facilitates the condensation of the seed into large bubbles and so allows them to escape, by which process the glass is "fined" or "plained." But fining is often helped by the presence of substances which at this stage liberate large bubbles of gas below the surface, such bubbles rising to the top of the metal and in their course dragging the smaller seed with them. Saltcake facilitates "fining" somewhat, since the sulphur dioxide from it is to some extent liberated at a later stage in the fusion. For good fining other substances than saltcake are needed. An old and fairly effective method is the use of organic materials, as potatoes, beets, pieces of moist wood, etc., for these, plunged into the molten glass, rapidly gasify, leaving very little residue, and the gases so formed (chiefly water vapour) effectively "bubble" the glass.

Ammonium Nitrate. (*Formula, NH_4NO_3 . Molecular weight, 80.*)—This substance has been used as a fining agent of recent years, particularly for optical glasses. Its advantages are that it entirely gasifies, and that it can be obtained fairly pure, and so free from harmful residues. Its method of use is generally to wrap it in wet paper and thrust it deep into the metal by means of a fork, when it vaporises rapidly.

Arsenious Oxide. (*Formula, As_2O_3 . Molecular weight, 396.*)—Arsenious oxide, which is also named arsenious acid, white arsenic, and arsenic (the last term being wrongly applied since it is the name of the parent element itself), has been supposed to have several functions in glass-making.

According to Tscheuschner,* the action of arsenious oxide in glass

* *Die Glasfabrikation, Dresden, 1885, p. 23.*

melting was partly mechanical, due to its volatility, the bubbles stirring up the glass, and partly chemical. Chemically, arsenious oxide might act as an oxidising agent, becoming reduced to elementary arsenic and, in consequence, being expelled in any case because of the volatility of this element. It also served to remove the colour due to the excessive addition of manganese dioxide. Dralle* expressed almost precisely the same views as Tscheuschner, adding that arsenious oxide was useful in reducing the excess colour due to small over-doses of selenium (see p. 133) as well as of manganese dioxide.

Since 1910, investigators, particularly in America, have challenged the orthodox views expressed above. S. R. Scholes† appears to have been the first to show that arsenious oxide was not expelled from the glass on melting, but that most of it was retained. He found that, both in a soda-baryta and also in a lead-potash glass, the greater part of the arsenious oxide added was retained in the glass, almost all in the quinquevalent state. About the same time F. Gelstharp‡ showed that in the case of a sample of plate glass which he analysed, 56 per cent. of the original arsenious oxide was left in the glass, all being present as As_2O_5 , and none as As_2O_3 , despite the fact that the glass melting was carried on under reducing conditions.

Allen and Zies,§ at a later date, found that not more than 30 per cent. of the arsenic passed from the glass, though it should be mentioned that in four of the five glasses they examined, nitre had been added to the batch.

The experience of the authors confirms these later views. It is doubtful whether arsenic, *per se*, has any value as a refining agent or flux when added. Further, it is liable under certain conditions to produce cloudy glass, it tends to make the colour of window glass unstable in sunlight,|| and also has a discolouring action during lampworking when small amounts of it are present in glass tubing.¶

The most valuable function of arsenic is its "corrective" action when used in conjunction with manganese dioxide or selenium for decolourising purposes, and many hold the view that arsenic has a decolourising action of its own.

Antimony Oxide, Sb_2O_3 , remains almost completely in the glass and has no value as a fining agent.

In regard to the use of arsenious oxide or of antimony oxide in lampworking glasses, Hodkin and Turner** have proved that both these oxides produce glasses easily discoloured on reworking, more so even than lead glasses.

* *Die Glasfabrikation*, 1911, vol. i., p. 186.

† *Trans. Amer. Cer. Soc.*, 1913, **15**, 585.

‡ *J. Ind. Eng. Chem.*, 1912, **4**, 16.

§ *J. Amer. Cer. Soc.*, 1918, **1**, 787.

|| C. J. BROCKBANK, *Trans. Amer. Cer. Soc.*, 1915, **17**, 222.

¶ F. W. HODKIN and W. E. S. TURNER, *J. Soc. Glass Tech.*, 1919, **3**, 158

** *J. Soc. Glass Tech.*, 1920, **4**, 158.

Reducing Agents.

These substances are added either to promote the incorporation of some batch-forming oxide, or to produce the requisite conditions for the formation of particular colours, in each case by extraction of oxygen from some component of the batch. In the former class we have the use of carbon (generally as coal or coke) for reduction of salt-cake or barium sulphate, in the latter the use of Rochelle salt or stannous oxide to obtain metallic copper from its compounds when copper ruby is desired. It must be emphasised that reducing agents cannot be employed in lead batches. Again, oxidising and reducing agents must not be employed together in the same batch, since they counteract one another. This prevents the use of nitre in saltcake batches.

(109) **Colouring Agents.**—If we include opal glass we may divide coloured glasses into the following groups: (1) Those produced by coloured silicates or other salts dissolved in the glass; (2) those obtained by a colloidal solution such as ruby glasses, and carbon, and possibly sulphur amber; (3) colours produced by a suspension of undissolved grains of appreciable size as stannic oxide opal and the aventurines; (4) colour produced by a solidified emulsion, as phosphate opal; (5) colour produced by devitrification such as cryolite opal.

Coloured Silicates and other Salts.—The first group results from the power of selective absorption which is exercised by certain silicate solutions (in common with other salts solutions), upon the rays of light traversing them, by virtue of which certain portions only of the spectrum composing white light are allowed to pass through. The colour of the glass containing the silicates is then complementary to the colour or colours absorbed. The depth of the colour and, to some extent, its quality is dependent upon the concentration of the silicate in the glass, or, if this be constant, upon the thickness of the glass. Fig. 5 (p. 37) is from a curve by Zsigmondy* showing the absorption of light by a glass containing cobalt silicate. It will be seen that the amount absorbed in the yellow and green portion of the spectrum is very large, but practically all the red and violet and much of the blue are transmitted.

Of the colours produced by metallic salts, the following are the most important:

Violet, nickel or manganese silicates.

Blue, cobalt or cupric silicates (the copper colour is greenish-blue).

Green, chromium or ferrous silicates.

Yellow, ferric or cerium silicates. Uranium compounds also give a yellow colour with a greenish fluorescence. Some sulphides—as, for instance, cadmium sulphide—produce characteristic yellow colours. Alkali chromates under suitable conditions give a yellowish-green colour to glass.

Amber, iron and manganese silicates in conjunction.

Grey or Smoked, manganese, iron and copper silicates together in certain proportions, or copper and nickel silicates.

* *Ann. d. Phys.*, 1901, 4, 60.

Black, high manganese content with some cobalt, copper or ferric silicates, or alternately chromium and ferric silicates.

It will be seen that some colours are obtained by the combination of two or more coloured salts, a method which admits of an almost unlimited variety of shades. A point of importance is that the colours produced by some oxides vary largely with the variation of the composition of the glass, as we shall see when we consider the colouring compounds in detail.

(110) **Nickel Compounds.**—Nickelous oxide, NiO , is a greenish-grey compound which can be obtained commercially. Nickelous hydroxide, Ni(OH)_2 , known from its colour as "nickel oxide, green," may be employed, the chief objection to it being that its moisture content is variable. Nickelic oxide, Ni_2O_3 , the commercial "black nickel oxide," when used, loses oxygen and gives nickelous salts. When pure it corresponds to about 90 per cent. of its weight of the lower oxide. The only stable salts in the glass are the nickelous salts. The colour due to nickel silicate in glass is fairly strong, 1 part of NiO per 1,000 of glass being quite appreciable. The colour, however, varies widely with the composition of the glass; in potash-lime glass the colour is reddish-violet, in soda-lime glass brownish-violet, in boro-silicate glass brown, and in lead silicate glasses red. Colours due to nickel are stable and not sensitive to oxidising or reducing agents. In soda-lime glasses a trace of cobalt used in conjunction with the nickel oxide gives a better colour. Glasses coloured by nickel compounds do not, in general, find wide application.

TABLE XXXVI.—BATCHES FOR GLASSES COLOURED BY NICKEL COMPOUNDS

	<i>Brownish-Purple.</i>	<i>Purple.</i>	<i>Yellowish-Purple.</i>
Sand	1,000	1,000	1,000
Soda-ash .. .	500	—	500
Potash .. .	—	650	—
Limespar .. .	250	250	250
Nickel oxide (black) .. .	7.25	7.25	4
Cobalt oxide . . .	—	—	0.1

(111) **Manganese Compounds.**—Manganese is universally added to the glass as—

Manganese Dioxide (*Formula, MnO_2 . Molecular weight, 87*), wrongly called manganese (the name of the parent metal). It is found as the mineral pyrolusite, ground samples of which are generally employed. The manganese dioxide content of pyrolusite is very variable and the amount of iron present may be high, so that a knowledge of the composition of the substance is essential.

The colours due to manganese vary with the state of oxidation, and the following series of compounds may be obtained: (a) from acidic oxides, permanganates of the composition R'MnO_4 corresponding to the

oxide, Mn_2O_7 , and purple in colour, manganates, $\text{R}'_2\text{MnO}_4$, corresponding to the oxide MnO_3 , and green in colour, manganites, $\text{R}'_2\text{MnO}_3$, corresponding to manganese dioxide MnO_2 ; (b) from basic oxides, manganic salts, derived from manganic oxide, Mn_2O_3 (as $\text{Mn}_2(\text{SO}_4)_3$); and manganous salts, from manganous oxide, MnO (as MnSO_4).

TABLE XXXVII.—BATCHES FOR LIME GLASSES COLOURED BY MANGANESE COMPOUNDS

	Reddish-Violet.*	Bluish-Violet.*	Brownish-Violet.†	Indigo Blue.*	Reddish-Brown †
Sand	1,000	1,000	1,000	1,000	1,000
Potash	300	300	—	300	—
Soda-ash	—	—	330	—	330
Nitre	60	60	—	60	—
Limespar	140	140	140	150	160
Manganese dioxide (iron-free)	40	40	140	30	112
Cobalt oxide	—	0.2	—	2	—
Iron oxide	—	—	10	—	—

	Grey.†	Black.			
		1†	2‡	3	4†
Sand	1,000	1,000	1,000	1,000	1,000
Potash	150	250	80	—	—
Soda ash	180	100	280	330	330
Limespar	140	130	160	200	150
Sodium uranate	15	—	—	—	—
Cobalt oxide	5	—	10	53	1
Nickel oxide	15	—	—	—	—
Manganese dioxide	10	230	200	200	220

Manganous salts are the most stable, the other compounds being easily reduced to this condition, and it is certain that manganous salts are colourless. By which of the other salts the characteristic colour due to manganese is produced is not certain. Not only are the higher oxide derivatives easily reduced, but, on prolonged heating, they slowly decompose with evolution of oxygen, and the ultimate production of colourless manganous salts. Hence the colour of manganese in glass depends upon the effect of unstable, easily reduced compounds, and it is greatly influenced by the conditions during melting, a batch containing reducing agents, or reducing furnace gases, destroying the colour, whilst prolonged founding produces the same effect. Zsigmondy found that the more acid

* HOHLBAUM, *Zeitgemässe herstellung, bearbeitung und verzierung des feineren Hohlglases*, Leipzig, 1910.

† SCHNURPFEL, *Die schmelzung der Hohl-, Schliff-, Press-, Tafel-, und Flaschengläser*, Leipzig, 1906.

‡ GERNER, *Die Glasfabrikation*, Leipzig, 1897.

in character is the batch (*i.e.*, the greater the proportion of silica), the more readily is oxygen evolved—so that glasses of fairly low silica content are preferable for the production of manganese colours. Frink* found that a smoky flame in the pot tended to produce a green colour, whilst oxygen converted the colour to a pink or violet. Tillotson states that the green colour due to manganates is always found when the glass is melting. From these observations it is highly probable that the colour produced by manganese is due to the presence of manganates and permanganates in the glass.

It may be pointed out that carbon can only be employed in a glass coloured by manganese to produce amber or black colours.

With potash-lime glasses an amethyst colour is obtained, the greatest absorption of light being in the green, whilst potash-lead and soda-lime glasses give a more reddish-violet colour. The colour of manganese glasses is often varied by the addition of a trace of cobalt. When present in large quantities manganese compounds colour the glass brown, and if the amount is extremely large an almost black colour is produced, at which stage the addition of some cobalt oxide, iron oxide, nickel oxide, or copper oxide produces a good black glass.

TABLE XXXVIII—BATCHES FOR LEAD GLASSES COLOURED BY MANGANESE COMPOUNDS.

					<i>Red-Violet.</i> †	<i>Blue-Violet</i> †	<i>Grey</i> ‡
Sand	1,000	1,000	1,000
Soda-ash	—	—	30
Potash	300	300	140
Red lead	620	620	160
Nitre	50	50	20
Manganese dioxide	26	26	20
Cobalt oxide	—	0.15	—
Iron oxide	—	—	10
Copper oxide	—	—	10

(112) **Cobalt Compounds.**—Cobalt oxide is used as a means of adding cobalt in glass. Cobalt salts are of two types, cobaltous, corresponding to the oxide CoO , and cobaltic, corresponding to Co_2O_3 , but only the former salts are stable in glass. The commercial oxide is really neither of the above, but it corresponds more closely with the formula Co_3O_4 . Cobalt in glass is an extremely powerful colouring agent, 1 part per 10,000 of glass producing an effective blue colour, whilst 1 part per 100,000 is quite distinct. For this reason little of the oxide is needed, and care must be taken to ensure even mixing in the batch. In some cases the cobalt is added in the form of smalt, a potassium silicate glass coloured by 2 to 7 per cent. of cobalt oxide, when a more even mixing can be obtained. Zaffre, an ignited, impure, cobalt earth, is not now largely employed.

The colour due to cobalt is very stable; it is "hard" in its nature

* *Trans. Amer. Cer. Soc.*, 1917, 19, 370

† HOHLBAUM, *loc. cit.*

‡ GERNER, *loc. cit.*

and may be toned by the addition of the oxides of copper, manganese, nickel, or ferric iron.

TABLE XXXIX.—BATCHES FOR GLASSES COLOURED BY COBALT COMPOUNDS.

	Lime Glasses.								Lead Glasses.	
	Bright Blue.				Dark Blue.				Bright Blue.*	Dark Blue.*
	1§	2*	3†	1‡	2*	3‡	4‡			
Sand ..	1,000	1,000	1,000	1,000	1,000	1,000	1,000	Sand ..	1,000	1,000
Potash ..	—	340	120	—	340	50	—	Potash ..	300	300
Soda-ash ..	380	—	200	350	—	280	350	Nitre ..	50	50
Limespar ..	240	170	140	150	160	160	140	Red lead ..	670	680
Cobalt oxide	2·85	3	1·6	2	4	1·8	—	Cobalt oxide	2	3
Smalt ..	—	—	—	—	—	—	85	Stannic oxide	7	—
Manganese dioxide	0·5	—	—	—	—	6	—			
Stannic oxide	—	10	—	—	—	—	—			

(113) **Copper Compounds.**—The colour due to cupric salts is greenish-blue, but the intensity is much less than that of the colours produced by cobalt compounds, 2 per cent. not being excessive for a good colour. Cupric silicate produces a fairly uniform colour in all glasses, the best results being obtained in the absence of iron. Copper compounds used are:

TABLE XL.—BATCHES FOR GLASSES COLOURED BY COPPER COMPOUNDS.

		Lime Glasses.							Lead Glasses.	
		Medical.	Blue-Green §	Aquamarine.						
				1‡	2*	3‡	4†	5‡		Aqua-marine.*
Sand ..	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	Sand ..	1,000
Potash ..	—	—	50	300	250	200	—	—	Potash ..	300
Soda-ash ..	330	330	250	—	80	140	280	—	Red lead ..	640
Limespar ..	160	128	160	140	130	140	160	—	Nitre ..	50
Copper oxide (CuO)	2	55	—	23	7·5	40	—	—	Copperoxide (CuO)	15
Copper sulphate	—	—	40	—	15	—	20	—		
Cobalt oxide	0·01	—	—	—	—	0·06	—	—		
Nitre ..	—	—	—	60	—	—	—	—		
Borax ..	—	—	—	—	—	20	—	—		

* HOHLBAUM, *loc. cit.*† GERNER, *loc. cit.*‡ SCHNURPFEL, *loc. cit.*§ BALDERMANN, *Der praktische Glashüttentechniker*, Leipzig, 1908.

|| Smalt.

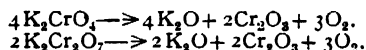
(a) Copper oxide, CuO , a black powder obtained by heating copper in air. It may be obtained commercially in a fairly pure form. Copper hammer-scale is an impure form and contains unoxidised copper.

(b) Copper sulphate, $\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$, also known as "blue vitriol," is sometimes employed. It corresponds to 28 per cent. of copper oxide. Cuprous compounds are mostly used for the production of copper ruby and will be described later. Occasionally cuprous oxide is used for green glasses.

(114) **Chromium Compounds.**—There are two types of chromium compounds—chromic salts, corresponding to the basic oxide Cr_2O_3 , and the salts of chromic acid, corresponding to the acidic oxide CrO_3 . The green colour in glass is produced by salts of the first type.

Chromic oxide, Cr_2O_3 , is sometimes used as a batch material. It is very infusible, and it is extremely difficult to incorporate evenly and completely in the glass. For simplicity of manipulation and evenness of colouring chromic acid compounds are widely used to produce the chromic green.

The most common salts are: *potassium chromate*, K_2CrO_4 , and sodium chromate, $\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O}$, yellow solids readily soluble in water, and the acid salts: *potassium dichromate*, $\text{K}_2\text{Cr}_2\text{O}_7$, and sodium dichromate, $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$. The dichromates are red in colour and not so easily dissolved as the chromates. The Cr_2O_3 equivalent of the various salts is K_2CrO_4 , 39.4 per cent.; $\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O}$, 22.2 per cent.; $\text{K}_2\text{Cr}_2\text{O}_7$, 52.7 per cent.; $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, 51 per cent. The simplest way of adding the salts is by pouring a solution of these over the batch. At fairly high temperatures the chromic acid salts decompose according to the following equations:



Lead chromate, PbCrO_4 , *barium chromate*, BaCrO_4 , and *copper chromate*, CuCrO_4 , are also used in special cases.

In general, the colour due to chromium compounds is green with a slight yellowish tint. It is well marked, but its intensity is less than that of cobalt. By using a glass melting at a low temperature the chromate may be only partially decomposed and a colour strongly inclining to yellow results. Little chromic oxide serves to saturate glass, and when the saturation limit is exceeded an aventurine is obtained.

Chrome saltcakes containing small amounts of chromium compounds are now frequently used for the production of chrome greens, chiefly for bottles. For regularity of colour the chrome content of the saltcake needs careful checking.

(115) **Uranium Compounds.**—Uranium trioxide, UO_3 , is a brownish-yellow powder and colours the glass yellow with a greenish fluorescence. It is an acid oxide, and its alkali salts may be used.

Sodium uranate, $\text{Na}_2\text{U}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$, is a yellow powder and is equivalent to about 84 per cent. of the oxide.

(116) **Iron Compounds.**—For the production of iron colours in glass, ferric oxide, Fe_2O_3 , the rouge of commerce, is employed.

The colour due to iron depends upon whether the metal is in the ferrous or ferric condition. With ferric iron present, which obtains when oxidising agents, as nitre, etc., are added to the batch, a yellow colour is obtained, whilst with ferrous compounds the colour is green. Dralle gives the colour of ferrous silicate as bluish-green, the range of colours varying from this, through green and greenish-yellow to yellow, as the proportion of ferric to ferrous salt increases. That such is the case is by no means certain; indeed many incline to the view that the bluish-green is an intermediate stage between the ferrous and ferric condition. The fact that the bluish-green colour is destroyed and a pure green is substituted when arsenious oxide is added to the batch seems to support

TABLE XLI.—BATCHES FOR LIME GLASSES COLOURED BY CHROMIUM COMPOUNDS

	* Soft Green.	† Dark Green.	‡ Sea Green.	Antique Green.			* Moss Green.		§ Chrome Green.
				1†	2†				
Sand ..	1,000	1,000	1,000	1,000	1,000	Sand ..	1,000	Sand ..	1,000
Potash ..	300	120	100	100	160	Potash ..	300	Soda-ash ..	330
Soda-ash ..	—	200	250	250	160	Limespar	160	Fluorspar	28
Limespar ..	160	140	140	150	140	Barium chromate	40	Limespar	166
Potassium dichromate	5	—	—	—	—	Nitre ..	60	Chromic oxide	0.65
Potassium chromate	—	10	1.5	6.5	6			Potassium chromate	0.45
Chromium oxide	—	10	—	—	—			Lead chromate	1.35
Copper oxide	1.2	20	—	9	10			Iron oxide	0.45
Iron oxide ..	1	10	27.5	9	10				
Nitre ..	60	—	—	—	—				
Borax ..	—	20	—	20	20				

TABLE XLII.—BATCHES FOR LEAD GLASSES COLOURED BY CHROMIUM COMPOUNDS

	* Soft Green.	* Rome Green.		* Moss Green.		§ Dark Green.
Sand ..	1,000	1,000	Sand ..	1,000	Sand ..	1,000
Potash ..	300	300	Potash ..	300	Potash ..	120
Red lead ..	670	650	Red lead ..	650	Soda-ash ..	240
Nitre ..	50	50	Nitre ..	50	Limespar ..	100
Potassium dichromate	3.34	—	Barium chromate	27	Red lead ..	20
Copper ..	1.2	4.7			Nitre ..	20
Iron oxide ..	0.7	—			Chromic oxide ..	10
Chromic oxide ..	—	5			Copper oxide ..	60
					Potassium chromate	20

* HOHLBAUM, *loc. cit.*
 ‡ SCHNURPFEL, *loc. cit.*

† GERNER, *loc. cit.*
 § BALDERMANN, *loc. cit.*

the latter theory, in so far as the arsenious oxide generally acts as a reducing agent. Again, the bluish-green colour often occurs in metal melted in tanks in which oxidising conditions obtain. With small quantities of iron, the ferrous silicate colour is the more prominent, but the ferric salt gives the more pronounced effect when the iron content is large. With a fairly appreciable colour the ferrous green is more pleasing and is to be preferred. Since iron compounds occur in most glass-making materials, particularly in sands, it is sometimes possible to choose materials which will give the required depth of colour to the glass. The usual use of iron for colouring glass is in conjunction with other colouring compounds.

(117) **Iron-Manganese Amber Glasses.**—When manganese dioxide and iron oxide are added to the same batch, glasses of a varying series of colours may be obtained, according to the relative amounts of the two oxides present, and also to the conditions of founding. The manganese dioxide has the effect of oxidising the iron and producing the ferric colour, the amount of oxidation depending upon the relative amounts of the two oxides present. The greenish-yellow colour due to iron and the purple or violet produced by the manganese are then superimposed.

TABLE XLIII.—BATCHES FOR GLASSES COLOURED BY URANIUM COMPOUNDS

Lime Glasses.

	Orange Yellow.		* Gold Green.		† Eleonor Green.		† Antique Green
Sand ..	1,000	Sand ..	1,000	Sand ..	1,000	Sand ..	1,000
Potash ..	120	Potash ..	300	Potash ..	100	Potash ..	80
Soda-ash ..	190	Soda-ash ..	—	Soda-ash ..	250	Soda-ash ..	250
Limespar ..	145	Limespar ..	175	Limespar ..	140	Limespar ..	140
Nitre ..	5	Nitre ..	60	Uranium oxide	3.5	Manganese dioxide	60
Uranium oxide	3	Sodium uranate	5	Chromic oxide	2.5	Iron oxide	30
Selenium ..	0.6	Copper oxide	1.2			Uranium oxide	0.3
Arsenious oxide	2.5						

Lead Glasses.

					* Gold Green.	† Anna Green
Sand	1,000	1,000
Potash	300	400
Nitre	50	—
Limespar	—	140
Red lead	670	40
Sodium uranate	3.34	14
Copper oxide	0.8	10

* HOHLBAUM, loc. cit.

† GERNER, loc. cit.

‡ SCHNURPFEL, loc. cit.

If the oxides are in small amounts (as we shall see in discussing decolourisers), a greyish glass results, but with larger amounts present it is possible to produce an amber glass. As an indication of the variation of colour Müller* gave the following results:

<i>Percentage of the Oxides Present.</i>		<i>Colour of Glass in Pots.</i>	<i>Colour of Glass in Tanks.</i>
<i>FeO.</i>	<i>MnO.</i>		
0.75	3.50	Fairly bright yellow	Greenish-yellow
1	2	Yellowish-green	Fiery green
2	2	Greenish-yellow	Strong green
2	4	Bright golden yellow	Yellowish-green
2.5	6.5	Bright brown	Clear without fire
1	7.8	Dark orange	Dirty without fire

The colour in the tanks was evidently due to reducing conditions which prevailed, and Dralleg† states that by the right use of the colouring oxides and corresponding management of the flame, the dark orange (Rhine-wine red) can be obtained better in tanks than in pots.

(118) **Colour Caused by Suspensions.**—In a true solution the particles of the solute approximate to molecular size, and by no means can they be detected by their visibility. When molecules gather together in groups of sufficient size to be seen we have not a solution but a suspension. Suspensions in liquids can be filtered off, or, if allowed to stand, the suspended matter will slowly settle to the bottom, a process which, in the case of suspensions of extremely fine particles, may take weeks to complete. Where the suspension occurs in glass which is cooled to solidify, the settling of the suspension is impossible, and we obtain the effects seen in the opals and aventurines. It is immaterial in such cases whether the substance has been actually in solution in the glass and has afterwards crystallised out in the process of devitrification, or whether it has never been dissolved, but the former are likely to give the more even and regular results. Phosphate opal is also of the type of a suspension, insoluble calcium phosphate being distributed in the form of liquid drops in the molten glass (exactly as is the fat in milk), the setting of the glass preventing any change in the form of the emulsion.

Aventurine Glasses.

Certain types of glass, not too acid in character, may become super-saturated with colouring oxides, particularly copper oxide and chromic oxide. Cooling under suitable conditions causes the excess to crystallise out and gives aventurine glasses.

Chrome Aventurine.—Hohlbaum states that good crystal glass with 15 to 20 parts of potassium dichromate, $K_2Cr_2O_7$, to each 100 parts of sand will give a chrome aventurine.

Copper Aventurine.—The most suitable glasses are those which contain little or no lead. The effect may develop only on reheating.

Alexander‡ says that, in the case of Batch 1 (Table XLV.), it should

* *Sprechsaal*, 1880, 212.

† *Die Glasfabrikation*, 1, 126.

‡ *Sprechsaal*, 1903, 36, 1484.

be melted as rapidly as possible and the glass may be opaque red, transparent dark red, or colourless (in the last case reheating is necessary).

TABLE XLIV.—BATCHES FOR CHROME AVENTURINE GLASSES.

	1*	2	3* (Blue)
Sand	1,000	1,000	1,000
Soda-ash	350	400	350
Fluorspar	150	—	150
Felspar	300	—	300
Barium carbonate	250	—	250
Potassium dichromate	120	160	100
Manganese dioxide	70	—	50
Cobalt oxide	—	—	5.0
Limespar	—	200	—

TABLE XLV.—BATCHES FOR COPPER AVENTURINE GLASSES.

	1*	2	3
Sand	1,000	1,000	1,000
Soda-ash	320	533	225
Potash	80	227	112
Limespar	320	238	100
Red lead	10	—	—
Cuprous oxide	60	—	—
Cupric oxide	—	83	50
Ferric oxide	—	—	75
Ferrous oxide	30	—	—
Stannic oxide	30	—	—
Nitre	—	133	—

(119) **Opal Glass**—(1) *Emulsion Opals*.—The first opal glasses produced were “bone glasses” in which bone ash was used for producing the effect. *Bone ash* is obtained by the calcination of bones (generally from meat-extract factories), after first treating with solvents, such as carbon disulphide, ether, or benzene, to remove the grease, and afterwards with steam under pressure to “degelatinise.” The ignited product contains 60 to 80 per cent. of calcium phosphate.

“Baker guano” is calcium phosphate in a finer state of division than bone ash, and having a fairly low iron content, thus it is sometimes preferred. Difficulty arises in using natural phosphates, since these are of uncertain composition, or difficult to decompose and often contain too much iron. Better than either of the above, since its composition is known with certainty, is calcium phosphate itself.

The tricalcium phosphate (formula, $\text{Ca}_3(\text{PO}_4)_2$, molecular weight, 310) is obtained by precipitation from a phosphoric acid solution by addition of excess of milk of lime. As sold commercially it is fairly pure and is

by far the most used compound for producing a phosphate opal. The amount required is 8 to 30 parts for every 100 of sand, a glass with low silica content needing less phosphate than one containing much silica. In small quantities it acts as a flux, but when in excess is refractory.

In place of the normal phosphate, acid calcium phosphate, CaHPO_4 , $2\text{H}_2\text{O}$, is occasionally used, and sometimes sodium phosphate, the composition of the commercial salt being $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$. Sodium phosphate is soluble in water, whereas calcium phosphate is insoluble.

The cause of the opacity of phosphate glass is that at lower temperatures two liquid phases of different composition separate—the smaller one taking the form of fine globules of calcium phosphate suspended in the main bulk of the molten glass. With increase of temperature the two phases become miscible and a clear liquid results. Hence, if a phosphate glass is heated too strongly and then rapidly chilled, no opalescence is obtained, but if the clear liquid is allowed to stand for some time at a lower temperature (*i.e.*, not very far above the melting-point) the two phases again separate and the milkiness reappears. It is evident that, since the opalescence is caused by suspended transparent drops, there will be little real loss of light, the rays merely being scattered. The following are various batches for the production of phosphate opal glasses:

TABLE XLVI.—BATCHES FOR PHOSPHATE OPAL GLASSES.

	1*	2†	3
Sand	1,000	1,000	1,000
Potash	450	100	300
Soda-ash	30	245	70
Calcium phosphate (bone ash)	260	220	300
Limespar	30	180	100
Nitre	15	20	—
Red lead	5	—	—
Arsenious oxide	15	—	—
Manganese dioxide	1	—	—
Borax	—	20	—

(2) *Solid Suspension Opals*.—When stannic oxide, SnO_2 , is added to a lime-glass batch it proves very insoluble and, on founding, unless the temperature is very high and the amount of the oxide small, much of it is left scattered throughout the glass as very fine particles—an opal glass is in this manner produced.

The second class of opals actually cut off the light rays, giving a dense white suitable for enamels.

(3) *Opals by Devitrification*.—Of devitrification opals there are two types:

(a) High silica, low lime glasses easily devitrify, throwing down silica. Alabaster glass is sometimes produced in this way. To induce devitrification powdered glass of similar composition is thrown into the

* *Sprechaal*, 1901, 34, 3.† *Ibid.*, 1919, 52, 30.

molten metal kept at the lowest possible temperature needed for working. Tscheuschner* quotes the following analysis of three such alabaster glasses:

		1	2	3
SiO ₂	80.90	79.51	82.30
Na ₂ O	—	—	5.60
K ₂ O	17.60	16.87	5.66
CaO	0.70	2.79	3.30
PbO	—	1.00	—
Al ₂ O ₃	0.80	—	3.20

(b) Fluorine compounds together with aluminium compounds also produce opal glasses. As examples, cryolite (sodium aluminium fluoride, Na₃AlF₆) itself acts as an opalising agent, as does a mixture of fluorspar and felspar, or sodium silicofluoride (Na₂SiF₆) with felspar or kaolin. In the case of cryolite, crystals of some unknown fluorine compound are spread throughout the glass. Where fluorides are employed together with aluminous earth, again there is uncertainty as to the deposit, possibly only felspar itself being thrown down. Smull† regards the precipitates as finely divided (probably colloidal) silica or alumina, or both of these. In density of whiteness this class lies between phosphate and stannic oxide opals.

It may be well to point out here that "opal" glass is usually understood as that which, whilst being semi-opaque, gives the transmitted light an opal or fiery colour, whilst "alabaster" glass diffuses the light without materially altering its colour.

TABLE XLVII.—BATCHES FOR THE PRODUCTION OF ALABASTER GLASSES.

	1‡	2§	3
Sand	1,000	1,000	1,000
Litharge	156	164.3	—
Red lead	—	—	560
Soda-ash	219	249.9	490
Nitre	55	92.5	50
Fluorspar	60	—	—
Cryolite	—	57.8	—
Sodium fluoride	—	—	75
Sodium chloride	55	—	50
Borax	12.5 to 25	23.1	—
Aluminium hydroxide	181.2	—	—
Aluminium oxide	—	173.5	225
Plaster of Paris	—	14.5	—
Felspar	—	—	1,200
Strontium sulphate	—	—	17.5
Antimony oxide	—	—	5

* *Handbuch der Glasfabrikation*, p. 546.

† *J. Soc. Chem. Ind.*, 1915, 34, 405.

‡ G. MACBETH, *U.S. Pat. No. 1,097,600*.

§ H. A. SCHNELLBACH, *U.S. Pat. No. 1,143,788*.

|| *U.S. Pat. No. 1,245,487*.

TABLE XLVIII.—BATCHES FOR OPAL GLASSES.

	1*	2*	3*	4*	* 5*	6†
Sand	1,000	1,000	1,000	1,000	1,000	1,000
Potash	160	—	200	200	200	—
Soda-ash	—	200	—	—	60	150
Red lead	—	400	200	—	—	—
Limespar.	80	—	—	—	80	—
Zinc oxide	60	—	—	—	—	—
Arsenious oxide .. .	10	10	—	10	—	—
Cryolite	150	—	—	80	120	80
Fluorspar	—	220	200	100	—	90
Felspar	—	190	200	120	—	180
Potassium nitrate .. .	—	—	—	—	30	—
Stannic oxide	—	—	—	—	—	40

Chlorides and Sulphates as Opalescing Agents.—In passing, we may point out that sulphates and chlorides may give rise to cloudy glasses when these are prepared from easily melted batches, such as a lead-potash batch. An amount of only about 0.25 per cent. of K_2SO_4 was found by Cauwood and Turner† to produce cloudiness, but 0.5 per cent. of KCl was needed to give the same effect. The opalescent glasses obtained from these reagents have little commercial value.

(120) **Colloidal Solutions.**—It is possible to have solid particles in a liquid of a size intermediate between those which form a true solution and those which give a mere suspension, the resulting state being known as a colloidal solution. The lines of demarcation between true and colloidal solutions on the one hand, and colloidal solutions and suspensions on the other are not clearly defined. Colloidal particles cannot be seen even with the most powerful microscope, they do not settle on standing, whilst they cannot be separated by filtration except by the use of special membranes, as for instance parchment, which contain much finer pores than filter-paper. If a beam of light is passed through a colloidal solution, however, and is observed from a position outside the path of the beam, the course of the light can be traced in the liquid by the scattering of light rays in all directions by the colloidal particles. The effect was first observed by Tyndall, who showed that if a true solution, free from dust particles, is used, no sign of the beam in the liquid is visible from points outside its path, the particles here being too small to reflect the rays of light. Zsigmondy made use of the Tyndall effect in observing a powerful beam of light, passing through a colloidal solution, by means of a microscope, the axis of which was placed at right angles to the beam. He was thus able to count the number of light-reflecting particles in the field of view, each one appearing as a minute spot of light in a dark field. The ultra-microscope (such was the name given to Zsigmondy's instrument) enabled the number of colloidal particles in the region of microscopic vision to be counted, due to their reflection of light

* *Die Glashütte*, 1907, **87**, 210, etc† SCHNURPFEL, *loc. cit.*‡ *J. Soc. Glass Tech.*, 1917, **1**, 187.

even though the particles themselves were invisible. Knowledge of the number of particles in a certain volume of colloidal solution, and of the weight of the colloid actually present in this volume, allowed the size of the particles to be determined. Actually the values so obtained are extremely small, and vary for different solutions even of the same substance. Heavy metals—e.g., gold, silver, copper—and elements such as sulphur can, by suitable means, be made to give colloidal solutions in water, and these solutions vary in colour, the colour being dependent upon the size of the particles. As with water, so in the case of glass, gold, silver, and copper give colloidal solutions, whilst of the non-metals selenium, carbon, and sulphur produce similar effects. Colours which are obtained are ruby in the case of gold, copper and selenium, yellow due to silver, and amber due to carbon and to sulphur. It must be borne in mind, however, that the colour is variable, depending upon the size and shape of the particles, finer division causing a more intensive colouring. For instance, gold may give colourless, red, rose, blue, or violet glasses according as to how it is treated. As distinct from the colloidal colours due to gold, silver, copper, and selenium, which require reheating of the glass to bring up the colour, carbon and sulphur strike the colour whilst the molten metal is in the pot or tank.

(121) **Gold Compounds.**—The original method of producing gold ruby was to add colloidal gold itself in the form of *Purple of Cassius*, a product obtained by the precipitation of gold from its solutions by means of stannous chloride. Purple of Cassius is almost pure gold, its only impurity being small amounts of stannic oxide (SnO_2). Since gold compounds decompose on heating, to give the metal it is only necessary to add a gold salt to the batch to produce the same effect, a most convenient salt being *auric chloride* (AuCl_3 or HAuCl_4), which is obtained when metallic gold is dissolved in aqua regia (hydrochloric acid 3 parts, nitric acid 1 part). The amount of gold needed is small—not more than 1 part by weight to 10,000 parts of glass, even 1 part per 50,000 producing a fine ruby. Addition of such small amounts causes difficulty in mixing with the batch, and it is better to mix thoroughly with a small portion of the sand before the latter is mixed with the rest of the batch. For ease and certainty of mixing it is best to saturate some of the sand with a dilute solution of gold chloride, obtained as above, which material then carries the gold in a finely divided state into the batch. When the glass is first worked the gold is either dissolved as a silicate or else in such extremely fine colloidal particles that it gives a colourless or, at the most, a straw-yellow coloured glass. Reheating causes the particles to grow in size and at a dull red heat the colour appears. Too strong heating will give too large particles, and a glass purple by transmitted light and brown by reflected light is obtained. Zsigmondy and Seidentopf have proved that the size of particles of gold in ruby glass is of the order of 10 to 20×10^{-6} mm. The best glass for producing a gold ruby is lead crystal. When crystallised gold chloride is used, the formula of this substance is HAuCl_4 , and 339 parts by weight of it are equal to 192 parts of metallic gold.

(122) **Copper Compounds** (for producing ruby glass).—Only recently has the ruby due to copper been correctly understood, but the colour is

TABLE XLIX.—BATCHES FOR GOLD RUBY GLASS.

	1*	2
Sand	1,000	1,000
Red lead	440	730
Potash	260	380
Borax	200	—
Bone ash	—	10
Gold chloride	0.36	0.7†

now known to be caused by colloidal copper, which is not so easily obtained as colloidal gold. In the first place, easily reduced and finely divided compounds of copper, such as, for instance, cuprous oxide (Cu_2O) or copper sulphide (cuprous oxide is a red substance, whilst copper sulphide is black), are best; and, secondly, some reducing agent such as potassium bitartrate ($\text{KHC}_4\text{H}_6\text{O}_6$), stannous oxide (SnO) or ferrous-ferric oxide (Fe_3O_4 , iron scale), must also be added to the batch. The batch should be one melting at a fairly low temperature, and oxidising conditions during founding should be avoided. Randau has stated that the copper must form 2 per cent. of the batch, but Köhl proved that the effect can be obtained by the use of copper compounds in which the copper forms only 0.02 per cent. of the total batch. A source of failure is the use of a too strongly basic batch, causing the precipitation of cuprous oxide, and giving a liver brown colour when viewed with reflected light. Below are given in Table L. several batches for producing copper ruby, the first being by Randau.

TABLE L.—BATCHES FOR COPPER RUBY GLASS.

Sand	1,000	1,000	1,000	1,000	1,000	1,000
Potash	—	200	300	300	320	280
Soda-ash	180	—	25	—	50	110
Limespar.. .. .	—	—	120	50	160	180
Red lead	—	300	—	200	—	—
Borax (calcined)	—	—	0.24	—	—	60
Cuprous oxide	—	—	—	4.5	6	—
Cupric oxide	150	3	—	—	—	10
Copper sulphide.. .. .	—	—	0.19	—	—	—
Stannous oxide	200	1	—	65	20	40
Nitre	—	—	—	—	—	40
Witherite	—	—	—	—	—	190
Iron oxide	100	—	—	—	—	—
Calcium phosphate	—	—	—	10	—	—
Potassium bitartrate	—	—	—	10	—	—
Sodium sulphide	—	—	0.26	—	—	—

* HOHLBAUM, *loc. cit.*

† Or 0.4 of gold dissolved in aqua regia and evaporated to dryness.

‡ *Thorpe's Dictionary.*

§ HALLER.

|| *German patent, 1882.*

The colour is only developed on reheating. Copper ruby is so intense that it is mostly employed for "flashing" colourless glasses. If an excessive amount of the copper compound is employed a copper aventurine glass may result.

(123) **Selenium Compounds.**—Selenium ruby glass is similar to gold and copper ruby, in that the element itself, in the colloidal state, produces the colour. Selenium resembles sulphur, in that it produces corresponding compounds. It is commonly obtained as (1) Selenium itself, a red or black powder; (2) sodium selenite, Na_2SeO_3 (containing 45.7 per cent. of selenium); and (3) sodium selenate, Na_2SeO_4 . The selenate is not easily reduced, but the selenite readily gives the element under reducing conditions, consequently selenium or sodium selenite is used as colouring agent, the selenite often being used in conjunction with arsenious oxide. Since selenium burns away to some extent, the selenite is the more certain for producing the ruby colour. Lead selenite is black, and tends to be formed when selenium is added to lead glasses; hence lead glasses are not suitable for the production of the selenium colour. Potash glass gives better results than soda glass, and a potash-zinc oxide-barium oxide glass is generally favoured for the production of the finest colour. It is essential that pure raw materials be used and an even furnace temperature maintained if the best results are to be obtained. The glass should be worked out as soon as possible after fining and standing off, whilst the working-out temperature should be kept as steady as possible. The colour, on first working, is at most a faint straw, and must be developed by reheating.

TABLE LI.—BATCHES FOR THE PRODUCTION OF SELENIUM RUBY GLASS.

1*		2†		3		4	
Sand ..	1,000	Sand ..	1,000	Sand ..	1,000	Sand ..	1,000
Soda ash ..	180	Potash ..	350	Potash ..	303	Soda ash ..	298
Potash ..	150	Limespar ..	120	Soda-ash ..	303	Slaked lime	277
Limespar ..	150	Selenium ..	1.5-2	Zinc oxide	212	Cadmium	13.5
Selenium ..	1			Cadmium sulphide	15.1	sulphide	
				Selenium ..	15.1	Selenium ..	1.04
				Borax ..	15.1		

Batches Nos. 3 and 4 are recommended by Kirkpatrick and Roberts,† No. 3 for a soft working glass, and No. 4 for a plate glass. According to these authors the two most essential steps in the manufacturing process are: (1) the pot must be securely stoppered during filling and fining periods to prevent the loss of selenium by volatilisation, and (2) the glass must be allowed to cool a sufficient length of time after gathering, usually from half to one minute. In pressed ware the colour was developed by heating, after pressing, for a period of 1 to 5 minutes at a temperature of 900° C. The ware blown in moulds sometimes developed its colour before, sometimes after, being placed in the lehr.

* SCHNURPFIL, *loc. cit.*† *Sprechsaal*, 1915, 48, 250.‡ *J. Amer. Cer. Soc.*, 1919, 2, 896.

(124) **Silver Compounds.**—Silver nitrate, AgNO_3 , is the simplest silver compound to use. Its advantage lies in that it can be added to the batch in the form of a solution, thus ensuring even distribution. On heating strongly this compound decomposes and leaves the metal in the free state in the glass. As with glasses containing gold, the product is at first colourless, but reheating brings out the yellow colour.

Silver chloride, AgCl , is a white solid insoluble in water, and it is precipitated by the addition of hydrochloric acid to a silver nitrate solution. Silver oxide, Ag_2O , is a dark brown powder, obtained by the action of strong alkalis on silver nitrate solution. It is very unstable, and gives metallic silver at as low a temperature as 250°C . The chloride and oxide are usually employed for the production of yellow stains on the surface of glass after working.

(125) **Sulphur Amber.**—Sulphur, when present in the batch in the elementary state, produces an amber colour, a pleasing effect being obtained when the sulphur forms about 0.5 per cent. by weight of the batch. The colloidal solution obtained "strikes" in the pot or tank, and needs no reheating. To produce the colour the element in the powdered form, *e.g.*, flowers of sulphur, is used. Sulphur must not be employed in lead glasses, since black lead sulphide is produced in such cases. Oxidising agents destroy the colour caused by sulphur.

TABLE LII.—BATCHES FOR SULPHUR AMBER GLASSES AND BATCH FOR GOLDEN YELLOW GLASS.

Amber Glasses.				Golden	
	1	2*			
Sand	1,000	1,000	Sand .. .	1,000	
Potash	—	100	Potash .. .	100	
Soda-ash	250	250	Soda-ash ..	240	
Saltcake	80	—	Limespar ..	180	
Limespar	225	160	Fluorspar ..	50	
Sulphur	15	15	Sulphur .. .	12.5	
Arsenious oxide ..	5	5			

(126) **Carbon Amber.**—Although the yellow colour produced by carbon has long been known, its use as a definite colouring agent dates only from about the middle of last century. Splitgerber believed that the amber colour was due to reduction of sulphur compounds by the carbon, and that where sulphur was absent the colour was not produced, a view which was shared by Dralle. Springer has produced a carbon amber with batches entirely free from sulphur—although the colour is much less intense than when sulphates are present. The best effect is obtained when carbon and sulphur are both added to the batch. The best type of glass for a carbon or a carbon-sulphur amber is a soft glass, high in alkali, for, with a more acid glass, the carbon tends to burn out. Too much carbon leads to excessive foaming in the batch during fusion.

* SCHNURPFEL, *loc. cit.*

TABLE LIII.—BATCHES FOR CARBON AMBER GLASSES.

1			2*			3		
Sand	1,000		Sand	1,000		Sand	1,000	
Soda-ash	380		Potash	400		Soda-ash	330	
Limestone.. ..	180		Limespar	170		Limespar	180	
Saltcake	8		Powdered coal	2 to 4		Graphite	3·5	
Carbon (coal or coke)	10							
Graphite	1							

TABLE LIV.—BATCHES FOR THE PRODUCTION OF A CARBON-SULPHUR AMBER GLASS.

							1	2
Sand							1,000	1,000
Soda-ash							350	305
Saltcake							—	14
Limespar							200	220
Carbon							6·0	4·5
Sulphur							4·0	1·5

(127) **Cadmium Sulphide** is sometimes employed for the production of, or the increase of intensity of, yellow glasses. It is a yellow powder and its formula is CdS .

TABLE LV.—EXAMPLES OF BATCHES CONTAINING CADMIUM SULPHIDE.

				Yellow.*					Canary† Yellow (Opal).
Sand				1,000	Sand				1,000
Potash				400	Potash				300
Limespar				170	Limespar				90
Cadmium sulphide				18	Red lead				150
Sulphur flowers				10	Nitre				50
					Borax				15
					Calcium phosphate.. ..				30
					Cadmium sulphide.. ..				30
					Rochelle salt				7·5
					Sodium sulphide				7·5

 * HOHLBAUM, *loc. cit.*

 † SCHNURPFEL, *loc. cit.*

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TABLE LII.—BATCHES FOR SULPHUR AMBER GLASSES AND BATCH FOR GOLDEN YELLOW GLASS.

Amber Glasses.			Golden Yellow Glass.		
	1	2*			
Sand	1,000	1,000	Sand	1,000	
Potash	—	100	Potash	100	
Soda-ash	250	250	Soda-ash	240	
Saltcake	80	—	Limespar	180	
Limespar	225	160	Fluorspar	50	
Sulphur	15	15	Sulphur	12.5	
Arsenious oxide ..	5	5			

(126) **Carbon Amber.**—Although the yellow colour produced by carbon has long been known, its use as a definite colouring agent dates only from about the middle of last century. Splitgerber believed that the amber colour was due to reduction of sulphur compounds by the carbon, and that where sulphur was absent the colour was not produced, a view which was shared by Dralle. Springer has produced a carbon amber with batches entirely free from sulphur—although the colour is much less intense than when sulphates are present. The best effect is obtained when carbon and sulphur are both added to the batch. The best type of glass for a carbon or a carbon-sulphur amber is a soft glass, high in alkali for, with a more acid glass, the carbon tends to burn out. Too much carbon leads to excessive foaming in the batch during fusion.

* SCHNURPFEL, *loc. cit.*

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TABLE LIIL.—BATCHES FOR CARBON AMBER GLASSES.

1			2*			3		
Sand	1,000		Sand	1,000		Sand	1,000	
Soda-ash	380		Potash	400		Soda-ash	330	
Limestone.. ..	180		Limespar	170		Limespar	180	
Saltcake	8		Powdered coal ..	2 to 4		Graphite	3.5	
Carbon (coal or coke)	10							
Graphite	1							

TABLE LIV.—BATCHES FOR THE PRODUCTION OF A CARBON-SULPHUR AMBER GLASS.

							1	2
Sand	1,000	1,000
Soda-ash	350	305
Saltcake	—	14
Limespar	200	220
Carbon	6.0	4.5
Sulphur	4.0	1.5

(127) **Cadmium Sulphide** is sometimes employed for the production of, or the increase of intensity of, yellow glasses. It is a yellow powder and its formula is CdS .

TABLE LV.—EXAMPLES OF BATCHES CONTAINING CADMIUM SULPHIDE.

				Yellow.*					Canary† Yellow (Opal).
Sand	1,000	Sand	1,000
Potash	400	Potash	300
Limespar	170	Limespar	90
Cadmium sulphide	18	Red lead	150
Sulphur flowers	10	Nitre	50
					Borax	15
					Calcium phosphate..	30
					Cadmium sulphide..	30
					Rochelle salt	7.5
					Sodium sulphide	7.5

* HOHLBAUM, *loc. cit.*

† SCHNURPFEL, *loc. cit.*

CHAPTER X

THE DECOLOURISING OF GLASS

(128) **Decolourising Agents.**—Iron compounds are found to some extent in almost all the materials used in making glass, whilst the attack on the refractories during founding further serves to add to the iron content of the glass. Very little ferrous silicate suffices to produce an unmistakable colour in the glass, and even the best glasses would have the characteristic green tint if some method were not provided for its elimination. In our survey of glass-making sands it was pointed out that it is customary to choose sands of low iron oxide content for the production of the better types of glassware, but this alone will not serve to free the glass from colour. Even glass made from the best sand procurable, that is, with an iron oxide content of less than 0.02 per cent., and other materials quite iron oxide free, shows a distinct colour when viewed in thick slabs, whilst glass containing ferrous silicate equivalent to 0.1 per cent. Fe_2O_3 is strongly coloured.

Reduction of the Colour by Oxidation.—When the amount of iron silicate present is not large, the colour can be reduced in intensity, to some extent, by oxidising the iron to the ferric state, the yellow colour due to the ferric salt being less noticeable than the green caused by an equivalent amount of ferrous silicate. If larger amounts of iron compounds are present, the change from ferrous to ferric silicate merely serves to accentuate the colour. It cannot be claimed that the method of oxidation decolourises the glass, for the faint yellow colour can still be noted, especially against a white background. The most suitable oxidising agents to convert the iron to the ferric condition are potassium and sodium nitrates.

Decolourisation by the Production of Complementary Colours.—Any two colours are complementary when, between them, they absorb all the rays comprising white light to an equal extent. The complementary colour to the ferrous silicate green is purple—a colour in which the red and violet rays are transmitted, but the green as partially absorbed. It is possible, by the addition of suitable colouring agents to the glass, to correct the ferrous green by superimposing on it a purple of equal intensity. If both colours are faint, the resultant glass is free from colour, but since the effect has been produced by the subtraction of light-rays all along the spectrum, the glass will not be so bright and transparent as if no colouring oxides were present. Indeed, with increasing amounts of the colours present the glass becomes dull and grey, a result which may be worse than the original defect. The limit at which decolourisation ceases to be

successful is when the glass contains iron silicate equivalent to 0.1 per cent. of Fe_2O_3 ; with larger amounts of iron compounds present it is better not to try to decolourise. In the following paragraphs the colouring agents which are used to produce the requisite complementary colour to that due to the presence of iron compounds in glass are discussed in detail.

(129) **Manganese Dioxide.**—The effect of this substance is twofold, that of oxidising and that of colouring. By its oxidising action it tends to convert the iron to the ferric condition, moving the point of maximum colour intensity towards the yellow. The colour due to manganese is, as we have seen, variable. The bluish-violet colour obtained with potash glass is more nearly complementary to the tint produced by the iron than the brownish-violet produced in soda glass. Consequently manganese is a more successful decolouriser in potash glass than in soda glass, a better effect being produced in the latter case by the further addition of a very small amount of cobalt oxide. As with the use of manganese dioxide for colouring purposes, difficulties occur when it is employed for decolourising, since reducing conditions during founding destroy the colour, whilst long continued heating has the same effect. For this reason the reheating which glassware receives in the lehr weakens the colour, and articles which, before annealing, appear to be perfectly decolourised, are generally somewhat green or "low" in colour on emerging from the lehr. It is necessary, then, to have the glass slightly on the pink or "high" side when worked, in order to produce a perfectly decolourised glass after annealing. Finished ware slightly "high" in colour can be improved by a second passage down the lehr, although this involves waste of time and money. It is obvious from its nature that manganese dioxide is a good decolouriser for lead glass, whilst results are more certain in the case of glass melted in pots than that made in tanks. It is quite possible, however, if care is taken, to use manganese dioxide as a decolouriser in tank furnaces, but the presence of carbon, as for instance when saltcake batches are employed, renders it useless by destroying its colour. The small amount of manganese needed for decolourising renders uniform distribution in the batch difficult, and care must be taken to ensure thorough batch mixing. The amount needed depends upon the iron content of the glass.

(130) **Selenium and Cobalt Oxide.**—Neither selenium nor cobalt oxide alone is sufficient to neutralise the green colour, since the former transmits more of the red rays only, and the latter more of the blue. Together, however, the two are very effective. Reducing conditions are needed for the production of selenium colour, and so its more successful application lies in tank furnaces, whilst lead glasses cannot be decolourised by selenium and cobalt oxides.

The presence of 30 to 50 times its weight of arsenious oxide saltcake is necessary in the case of decolourisation with selenium. The slight tint given by the selenium is sufficiently strong without reheating, indeed the reheating in the lehr may tend to intensify the colour and produce a glass on the "high side."* Selenium is added either as the element itself or as sodium selenite. The amount of the element needed

* The final colour of the glass depends upon the temperature conditions of the lehr.

is small; it depends, of course, upon the ferrous silicate content of the glass, but generally it will be found to be in the neighbourhood of 1 part of selenium from 32,000 to 64,000 parts of sand, or $2\frac{1}{4}$ parts of sodium selenite (Na_2SeO_3), for the same amount of sand. The cobalt oxide needed is about one-sixth of this amount. The quantity given serves only with batches free from saltcake. Replacement of only a small amount of soda-ash by saltcake increases the amount of selenium needed,* but it has no effect on the cobalt oxide, which is the same in amount for all batches either with or without sodium sulphate. As with manganese dioxide, the incorporation with the batch must be thorough, and in this case it is better to grind the decolouriser well with some sand, and add the mixture to the batch.

(131) **Nickel Oxide.**—Because of the fact that nickel silicate is not as sensitive to oxidising and reducing conditions, it is sometimes used, particularly in Germany, instead of manganese dioxide, for decolourising purposes. Although fairly good, it does not give a perfect complementary colour, especially with soda glasses. In some cases it is added in place of cobalt oxide along with selenium, but here again with doubtful advantage. A usual method of using nickel oxide for soda glasses is with 5 to 7 per cent. of its weight of cobalt oxide.

* COUSEN and TURNER, *J. Soc. Glass Tech.*, 1922, 6, 168.

CHAPTER XI

CALCULATIONS FOR GLASS-MAKING

(132) **Regulation of the Composition of Glass Batches and of Glass.**—Too little attention has been given in the past to the proper regulation of the composition of the batches for producing glass. Although manufacturers have, in general, realised that uniformity of composition was desirable, their efforts in this direction have been often crude and unsystematic. Recent investigations of the variation of the properties of glass with its composition have shown how necessary it is, if regularity in the product is desired, that the glass should be kept within narrow limits of composition. This is the more important particularly when mechanical appliances are used for working the glass, machines for pressing or blowing, or feeding devices for supplying the molten glass to the machine. Here a slight variation of composition is sufficient to throw the finely regulated instrument out of action, since, whenever differences of viscosity and rate of setting of the glass occur, corresponding adjustments of the machine are necessary—alterations which can only be carried out within certain limits, and which also are often impossible to perform when the machine is operating. It is thus much more economical, and the rate of output is largely increased, if the composition of the metal remains steady throughout, allowing the machine to run continuously without readjustment.

Where the working of the glass is performed entirely by manual labour, the composition need not be kept quite so steady, since a workman can fairly readily adapt himself to the changing physical state of the metal. But even in this case unsuitable glass is fairly easily produced. On the one hand, too much alkali may be added, producing a soft and easily worked metal, but one which will easily be weathered, an alkali oxide content of over 18 per cent. giving a poor glass; on the other hand, high silica or lime may give a glass easily devitrifying and resulting in a stony metal. To guard against the above defects, the remedy is to supply a batch which will give a glass of constant composition, and this can only be accomplished by a knowledge of the nature of each batch constituent, and of the amount of each entering the glass. To obtain the desired information three things must be known, (1) the weight of each constituent of the batch, (2) the proportion of glass-forming oxides in each substance used, when pure, and (3) the purity of the materials used. With a knowledge of all three factors, not only can the composition of the glass be kept steady, but, whenever necessary, changes in composition in any direction can be made, as desired, and the new glass can again be

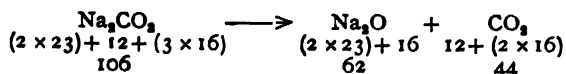
kept constant in composition. Further, the source of any glass-forming oxide can be changed, as for instance, when limestone is substituted for slaked lime as a source of calcium oxide, without alteration of the composition of the glass. In short, the foregoing three factors produce the key for any desired regulation of the composition of the glass.

(133) **The Amount of the Materials Used.**—No exact regulation of the batch or glass can be made unless the weight of each batch constituent is determined. For this purpose two methods are available, the first that of directly weighing the substances used, the second the indirect method of measuring out the materials by volume. For the former method a large weighing machine is necessary for the bulk of the batch components, but for such materials as decolourisers or colouring agents a smaller balance of greater delicacy will be required. Sometimes the batch-mixer, even when supplied with a weighing machine, neglects its use when not overlooked, and it should be insisted upon that not only are the materials weighed, but also that the amounts taken are entered up into a log-book before the substances are removed from the scale. The most crude volume methods consist in measuring by shovelfuls or barrowfuls, processes liable to large errors even when carefully carried out. Greater refinement is obtained by the use of a box or similar receptacle which can be filled with material and the top then smoothed. Here two errors may creep in. In the first place, different samples of the same material may differ considerably in density, as, for instance, light and heavy soda-ash, so that equal volumes may not always give equal weights. Again, the packing to which the material is subjected in the box may vary, with a consequent variation of the amount held.

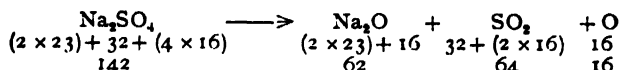
The volume method, however, if carefully carried out, gives fairly concordant results. Alterations of the amounts of the constituents used are not made so easily by the volume method as by the weight method. Finally, it must be pointed out that the packing which materials can undergo is appreciably affected by their moisture contents. In the case of sand, addition of water up to about four per cent. causes a decrease in the amount of sand which can be packed in a vessel, a decrease out of all proportion to the amount of water added. After this point, the variation of moisture content over a range of several per cent. causes practically no change in the weight of the sand which can actually be packed. Thus in the range of moisture content usual in practice, a box will always hold almost exactly the same *weight of sand*, even though the moisture content is somewhat variable.

(134) **The Amounts of Glass-forming Oxides obtained from Batch Materials.**—Let us assume, in the first place, that all materials are pure. Instead of considering glass as a complex mixture of silicates, we will regard it in the light of the constituent oxides present. For instance, simple soda-lime-silica glasses can be regarded as compounds of sodium oxide, calcium oxide and silica in varying proportions—the three together giving the sum-total of the glass produced. All the sand used remains in the glass either in the form of silicate or dissolved silica (if we neglect any material mechanically removed by the blast, etc.); 100 per cent. of the sand therefore enters the glass. Where sodium carbonate is used for providing the alkali the only portion left in the glass is sodium oxide,

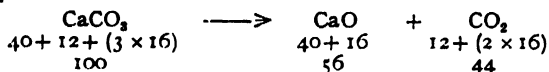
the carbon dioxide being completely eliminated. The relative weights of the soda-ash used and of the sodium oxide and carbon dioxide produced can readily be calculated from the equation of decomposition and a table of atomic weights. It will be:



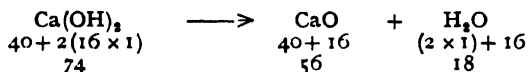
Every 106 parts of pure soda-ash will give 62 parts of sodium oxide in the glass, or $\frac{62}{106} \times 100 = 58.5$ per cent. of the weight of the sodium carbonate. Saltcake also gives sodium oxide:



The same amount of sodium oxide (62 parts) is obtained from 142 parts of saltcake as is obtained from the 106 parts of soda-ash—the percentage weight of sodium oxide in the saltcake being $\frac{62}{142} \times 100 = 43.7$. Where calcium carbonate is employed the amount of calcium oxide entering the glass is:



and the percentage amount of calcium oxide from the limestone is evidently 56. Quicklime itself enters completely into the glass, whilst slaked lime decomposes as follows:



The amounts of the three lime-producing substances which are equivalent to one another are evidently: 100 parts by weight $\text{CaCO}_3 \equiv 56\text{CaO} \equiv 74\text{Ca(OH)}_2$. Below we append a table (Table LVII.) of the more common batch constituents and details of the decomposition of each. It must be borne in mind that some substances never approach constancy of composition, examples of this being red lead, felspar, kaolin, hydrated alumina, and dolomitic limestone. In cases such as these an analysis of the material is required. As an example of the use of the factors given in column 7 of the table, if we wish to know the amount of potassium oxide entering the glass from, say, 450 lbs. of pure potash, it will be $450 \times 0.681 = 306.4$ lbs. of the oxide.

(135) **Purity of Materials.**—The purity of commercial materials is generally variable, and it cannot be too often insisted that a check should be kept upon the composition of substances used, by regular and systematic analysis. Where impurities occur, they may also enter into the composition of the glass, in which case modifications may be needed in the amounts of other batch materials required. Once the percentage composition of a substance is known the estimation of the amount of glass-forming oxides which will be obtained from it can readily be performed.

TABLE LVI.—PROPORTION BY WEIGHT OF BATCH MATERIALS WHICH ENTER THE GLASS.

1	2	3	4	5	6	7
<i>Material.</i>	<i>Formula.</i>	<i>Molecular Weight.</i>	<i>Oxide Molecules Entering Glass.</i>	<i>Total Molecular Weight of Oxides.</i>	<i>Ratio Weight of Oxide Weight of Material</i>	<i>Conversion Factor.</i>
Calcined alumina..	Al_2O_3	102.2	Al_2O_3	102.2	$\frac{102.2}{102.2} =$	1.00
Hydrated alumina	$\text{Al}_2(\text{OH})_6$	156.2	Al_2O_3	102.2	$\frac{102.2}{156.2} =$	0.654
Kaolin	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$	258.8	Al_2O_3	102.2	$\frac{102.2}{258.8} =$	0.395
			2SiO_2	$2(60.3) = 120.6$	$\frac{120.6}{258.8} =$	0.465
Potash felspar ..	$\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$	558.1	K_2O	94.1	$\frac{94.1}{558.1} =$	0.169
			Al_2O_3	102.2	$\frac{102.2}{558.1} =$	0.183
			6SiO_2	$6(60.3) = 361.8$	$\frac{361.8}{558.1} =$	0.648
Barium carbonate	BaCO_3	197.4	BaO	153.4	$\frac{153.4}{197.4} =$	0.777
Barium sulphate ..	BaSO_4	233.4	BaO	153.4	$\frac{153.4}{233.4} =$	0.657
Boric acid	H_3BO_3	62	$\frac{1}{2}\text{B}_2\text{O}_3$	$\frac{70}{2} = 35$	$\frac{35}{62} =$	0.564
Borax (crystallised)	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	382	Na_2O	62	$\frac{62}{382} =$	0.162
			$2\text{B}_2\text{O}_3$	140	$\frac{140}{382} =$	0.366
Borax (anhydrous)	$\text{Na}_2\text{B}_4\text{O}_7$	202	Na_2O	62	$\frac{62}{202} =$	0.307
			$2\text{B}_2\text{O}_3$	140	$\frac{140}{202} =$	0.693
Quicklime	CaO	56.1	CaO	56.1	$\frac{56.1}{56.1} =$	1.00
Slaked lime	$\text{Ca}(\text{OH})_2$	74.1	CaO	56.1	$\frac{56.1}{74.1} =$	0.757
Limestone	CaCO_3	100.1	CaO	56.1	$\frac{56.1}{100.1} =$	0.560
Calcium phosphate	$\text{Ca}_3(\text{PO}_4)_2$	310.3	3CaO	$3(56.1) = 168.3$	$\frac{168.3}{310.3} =$	0.542
			P_2O_5	142	$\frac{142}{310.3} =$	0.458
Fluorspar	CaF_2	78.1	CaO	56.1	$\frac{56.1}{78.0} =$	0.718
Red lead	Pb_3O_4	685.3	3PbO	669.3	$\frac{669.3}{685.3} =$	0.977
Litharge	PbO	223.1	PbO	223.1	$\frac{223.1}{223.1} =$	1.00

TABLE LVI.—PROPORTION BY WEIGHT OF BATCH MATERIALS WHICH ENTER THE GLASS—*Continued.*

1	2	3	4	5	6	7
<i>Material.</i>	<i>Formula.</i>	<i>Mole- cular Weight.</i>	<i>Oxide Molecules Entering Glass.</i>	<i>Total Molecule Weight of Oxides.</i>	<i>Ratio Weight of Oxide Weight of Material</i>	<i>Con- version Factor.</i>
Magnesia (calcined)	MgO	40.3	MgO	40.3	$\frac{40.3}{40.3} =$	1.00
Magnesium car- bonate	MgCO ₃	84.3	MgO	40.3	$\frac{40.3}{84.3} =$	0.478
Dolomite	MgCO ₃ .CaCO ₃	184.4	{ MgO CaO	40.3	$\frac{40.3}{184.4} =$	0.218
				56.1	$\frac{56.1}{184.4} =$	0.304
Potassium nitrate	KNO ₃	101.1	$\frac{1}{2}$ K ₂ O	$\frac{1}{2}(94.1)$ = 47.05	$\frac{47.05}{101.1} =$	0.465
Potash	K ₂ CO ₃	138.1	K ₂ O	94.1	$\frac{94.1}{138.1} =$	0.681
Soda-ash	Na ₂ CO ₃	106	Na ₂ O	62	$\frac{62}{106} =$	0.585
Saltcake	Na ₂ SO ₄	142	Na ₂ O	62	$\frac{62}{142} =$	0.437
Sodium nitrate ..	NaNO ₃	85	$\frac{1}{2}$ Na ₂ O	$\frac{1}{2}(62)$ = 31	$\frac{31}{85} =$	0.365
Sodium phosphate (crystallised)	Na ₂ HPO ₄ .10H ₂ O	322	Na ₂ O	62	$\frac{62}{322} =$	0.193
			$\frac{1}{2}$ P ₂ O ₅	$\frac{1}{2}(142)$ = 71	$\frac{71}{322} =$	0.220
Silica	SiO ₂	60.3	SiO ₂	60.3	$\frac{60.3}{60.3} =$	1.00
Zinc oxide ..	ZnO	81.4	ZnO	81.4	$\frac{81.4}{81.4} =$	1.00

For instance, to take the foregoing example once more, the amount of potassium oxide given by 450 lbs. of potash which contains only 94 per cent. K₂CO₃ is evidently $450 \times \frac{94}{100} \times 0.681 = 288.1$ lbs. The following further example will serve to make the point clearer, the first column giving the percentage composition of a soda-ash, of which 320 lbs. are used, and the third column the amounts of the oxides entering the glass.

<i>Soda-ash.</i>	<i>Per Cent.</i>	<i>Oxide entering Glass.</i>	<i>Lbs.</i>
Sodium carbonate (Na ₂ CO ₃) ..	95.4 ..	$320 \times 0.954 \times 0.585$ Na ₂ O =	178.6 ..
Sodium sulphate (Na ₂ SO ₄) ..	1.8 ..	$320 \times 0.018 \times 0.437$ Na ₂ O =	2.5 ..
Sodium chloride (NaCl) ..	0.4 ..	Practically completely vola- tilised	
Alumina (Al ₂ O ₃)	0.2 ..	320×0.002 Al ₂ O ₃ =	0.64 ..
Ferric oxide (Fe ₂ O ₃)	0.1 ..	320×0.001 Fe ₂ O ₃ =	0.32 ..
Loss on ignition (H ₂ O, etc) ..	2.0		
Total ..	99.9		

Below are given several typical calculations of use in preparing batches for various types of glass.

(136) **To Obtain a Batch for the Production of Glass with the Oxides in Particular Ratio.**—*Example 1.*—It is desired to produce a glass of the type suitable for machine worked glass, that is, of a molecular formula $1.2\text{Na}_2\text{O}$, 0.8CaO , 6SiO_2 using sand, limestone, and soda-ash. Here we see that:

<i>Parts by Weight.</i>					
6.0 molecules of SiO_2	are from	6.0 molecules of sand	$= 6.0 \times 60 = 360$		
1.2	"	Na_2O	"	1.2	" $\text{Na}_2\text{CO}_3 = 1.2 \times 106 = 127$
0.8	"	CaO	"	0.8	" $\text{CaCO}_3 = 0.8 \times 100 = 80$

Converting to usual type of batch mixture where 1,000 parts of sand are taken:

Sand	$= 1000$
Soda-ash	$= \frac{127 \times 1000}{360}$		$= 353$
Limestone	$= \frac{80 \times 1000}{360}$		$= 222$

If we desire to replace 5 per cent. of the soda-ash by an equivalent molecular weight of saltcake the number of molecules of soda-ash is now $\frac{1.2 \times 95}{100} = 1.14$, and of saltcake is $\frac{1.2 \times 5}{100} = 0.06$. The calculation now becomes:

Molecules. *Molecules.*

6.0 SiO_2	from 6.0 sand	$- 6 \times 60 = 360$	converted to sand	$- 1,000$
0.8 CaO	"	$0.8 \text{ CaCO}_3 = 0.8 \times 100 = 80$	"	limestone $= 222$
1.14 Na_2O	"	$1.14 \text{ Na}_2\text{CO}_3 = 1.14 \times 106 = 120.6$	"	soda-ash $= 335$
0.06 Na_2O	"	$0.06 \text{ Na}_2\text{SO}_4 = 0.06 \times 142 = 8.5$	"	saltcake $= 24$

Example 2.—Conversely the molecular composition of a glass can be found when made from a known batch mixture. By dividing the absolute weight of each batch constituent by its molecular weight the relative numbers of molecules present are obtained, from which the relative numbers of molecules of the oxides can easily be found. Take, for instance, a batch of the composition sand 1,000, soda-ash 300, limespar 250, potassium nitrate 30—

<i>Batch.</i>	<i>Relative Number of Molecules Present.</i>	<i>Number of Molecules of Oxide from 1 Molecule of Batch Material.</i>	<i>Relative Number of Oxide Molecules Present.</i>	<i>Converted Oxide Ratio.</i>
SiO_2 1000 ..	$\frac{1000}{60} = 16.67$	1	16.67	$= 6.00 \text{ SiO}_2$
CaCO_3 250 ..	$\frac{250}{100} = 2.50$	1	$2.50 \therefore \frac{2.50 \times 6}{16.67}$	$= 0.90 \text{ CaO}$
Na_2CO_3 300 ..	$\frac{300}{106} = 2.83$	1	$2.83 \therefore \frac{2.83 \times 6}{16.67}$	$= 1.02 \text{ Na}_2\text{O}$
KNO_3 30 ..	$\frac{30}{101} = 0.30$	$\frac{1}{2}$	$0.15 \therefore \frac{0.15 \times 6}{16.67}$	$= 0.05 \text{ K}_2\text{O}$

and the molecular composition of the glass will be 6.00SiO_2 , 0.90CaO $1.07\text{R}_2\text{O}$ (where R_2O represents total $\text{Na}_2\text{O} + \text{K}_2\text{O}$).

In the above calculations it is assumed that the materials are pure; impure materials will cause a modification of the calculation.

(137) To Find the Molecular Ratio of a Glass of Given Composition.—

Example 3.—Consider a Bohemian glass of the following percentage composition:

SiO_2	75.34
Al_2O_3	1.16
Fe_2O_3	0.02
CaO	7.25
MgO	0.14
K_2O	11.53
Na_2O	4.80
Total						100.24

The relative numbers of the molecules present are obtained by dividing the weight of each oxide by its molecular weight.

	Relative Number of Molecules.	By Conversion.	Ratio.	
			Formula A.	Formula B.
SiO_2	$\frac{75.34}{60} = 1.256$	$= 6.00$	6.00 SiO_2	9.52 SiO_2
Al_2O_3	$\frac{1.16}{102} = 0.011$	$\frac{0.011 \times 6}{1.256} = 0.05$	—	—
Fe_2O_3	—	—	—	—
CaO	$\frac{7.25}{56} = 0.129$	$\frac{0.129 \times 6}{1.256} = 0.62$	} 0.63 RO	} 1.00 RO
MgO	$\frac{0.14}{40} = 0.003$	$\frac{0.003 \times 6}{1.256} = 0.01$		
K_2O	$\frac{11.53}{94} = 0.123$	$\frac{0.123 \times 6}{1.256} = 0.59$	} $0.96 \text{ R}_2\text{O}$	} $1.52 \text{ R}_2\text{O}$
Na_2O	$\frac{4.80}{62} = 0.077$	$\frac{0.077 \times 6}{1.256} = 0.37$		

The alumina and iron oxide are ignored in working out the molecular ratio. The second formula (B) is obtained from A by multiplying throughout by $\frac{1.00}{0.63}$.

Example 4.—To find the molecular formula of a crystal glass having the following percentage composition:

SiO_2	54.25
PbO	33.38
$\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$	0.14
CaO	0.08
MgO	0.16
Na_2O	1.76
K_2O	10.30
MnO	Trace
Total						100.07

	Relative Number of Molecules.	By Conversion.	Ratio.	
			A.	B.
SiO ₂	$\frac{54.25}{60} = 0.904$	$= 6.00$	6.00 SiO ₂	5.77 SiO ₂
PbO	$\frac{33.38}{223} = 0.150$	$\frac{0.150 \times 6}{0.904} = 1.00$	1.04 RO	1.00 RO
Al ₂ O ₃ , Fe ₂ O ₃ and MnO	—	—		
CaO	$\frac{0.08}{56} = 0.001$	$\frac{0.001 \times 6}{0.904} = 0.01$		
MgO	$\frac{0.16}{40} = 0.004$	$\frac{0.004 \times 6}{0.904} = 0.03$	0.93 R ₂ O	0.89 R ₂ O
Na ₂ O	$\frac{1.76}{62} = 0.028$	$\frac{0.028 \times 6}{0.904} = 0.19$		
K ₂ O	$\frac{10.30}{94} = 0.110$	$\frac{0.110 \times 6}{0.904} = 0.74$		

(137a) **The Calculation of Batch Recipes to Produce a Glass of Given Composition.**—*Example 5.*—It is required to find a batch or batches which will produce glass of the percentage composition:

SiO ₂	71.43
Al ₂ O ₃	1.52
Fe ₂ O ₃	0.12
CaO	10.63
MgO	2.39
Na ₂ O	13.72
Total	99.81

It is evident that the iron oxide has been added unintentionally, that is, as an impurity of the batch materials, and its presence can be ignored. The alumina and magnesia were possibly also impurities in the original glass, but they are in such amounts that they must be included in the batch to be mixed.

SILICA.—If added as a high-grade sand, practically the same amount will be required. That is, for every 99.81 parts of glass produced, 71.43 parts of sand will be required.

ALUMINA.—This could be added as calcined alumina, in which case 1.52 parts would be required in the production of 99.81 parts of glass. When hydrated alumina is employed, an analysis of the material showing the amount of Al₂O₃ which it contains must first be obtained. If added as pure kaolin which contains 39.5 per cent. of alumina we should require $\frac{1.52 \times 100}{39.5} = 3.85$ parts. In this case silica would also be added (kaolin

contain, 46.5 per cent. of silica) to the extent of $\frac{3.85 \times 46.5}{100} = 1.79$ parts, so that the amount of sand necessary would be reduced to 71.43 - 1.79 = 69.64 parts. The alumina could not be added as potash felspar since the glass contains no potassium oxide.

LIME.—If added as quicklime 10.63 parts are required. The amount of slaked lime would be $\frac{10.63 \times 74}{56} = 14.04$ parts, and of limespar $\frac{10.63 \times 100}{56} = 18.98$ parts.

MAGNESIA.—Calcined magnesia to the extent of 2.39 parts are needed. The amount of magnesium carbonate would depend upon its MgO content, which is variable. Dolomite is often used as a source of magnesia and the amount needed would be $\frac{40}{40} = 10.93$ parts (approximately, since dolomite is distinctly variable in composition). Addition of dolomite would result in the presence of $\frac{10.93 \times 56}{184} = 3.32$ parts of calcium oxide in the glass, and the amount of quicklime would be reduced to $10.63 - 3.32 = 7.31$ parts, or of limestone to $\frac{7.31 \times 100}{56} = 13.06$ parts.

SODIUM OXIDE.—When soda-ash is employed the amount used will be $\frac{13.72 \times 106}{62} = 23.40$ parts. Saltcake requires $\frac{13.72 \times 142}{62} = 31.39$ parts, with also an addition of 5 per cent. or $\frac{31.39 \times 5}{100} = 1.57$ parts of carbon for reducing purposes.

From the above figures we can build up a series of batches each of which would give the required result. Two such batches (1 and 2) are given, and also the figures when the same batches are expressed in terms of 1,000 parts of sand.

	1	1a	2	2a
Sand	71.43	1,000	69.64	1,000
Calcined alumina	1.52	21.3	—	—
China clay	—	—	3.85	55.3
Quicklime	10.63	148.8	—	—
Limestone	—	—	13.06	187.6
Calcined magnesia	2.39	33.4	—	—
Dolomite	—	—	10.93	156.9
Soda ash	23.40	327.6	—	—
Saltcake	—	—	31.39	450.7
Carbon	—	—	1.57	22.5

Example 6.—A batch is required for producing a crystal glass with the following percentage composition:

SiO ₂	54.62
PbO	33.15
Fe ₂ O ₃ + Al ₂ O ₃	0.14
CaO	0.08
MgO	0.11
Na ₂ O	1.26
K ₂ O	10.45
MnO	0.02
Total	99.83

To produce 99.83 parts of glass the following ingredients are necessary:

(a) SAND.—Good quality sand, 54.62 parts.

(b) LEAD OXIDE.—Good red lead, the amount of which depends upon its composition. If a sample equivalent to 98.63 per cent. PbO is used $33.15 \times 100 = 33.61$ parts are added.

98.63

Oxides of iron, aluminium, calcium, and magnesium are small in amount and may be neglected.

(c) SODIUM OXIDE.—The soda-ash required is $\frac{1.26 \times 106}{62} = 2.15$ parts.

(d) POTASSIUM OXIDE.—The potash required is $\frac{10.45 \times 138}{94} = 15.34$ parts.

(e) MANGANESE OXIDE.—Good pyrolusite is added as a decolouriser in slight excess of the amount indicated by analysis. Actually the amount needed would depend upon the iron oxide present, the temperature and duration of the found, etc., and it could only be judged by experience. The amount required is about 0.05 parts.

The batch can now be written down as before:

	1	1a	2
Sand	54.62	1,000	1,000
Red lead (98.63 per cent) ..	33.61	615.3	615.3
Soda-ash	2.15	39.3	39.3
Potash	15.34	280.8	260.3
Nitre (KNO ₃)	—	—	30
Pyrolusite.. .. .	0.05	1.0	1.0

It is usual to add potassium nitrate to a batch of this type in order to maintain oxidising conditions, and since 2 molecules or 202 parts of nitre produce the same amount of potassium oxide as 1 molecule or 138 parts of potash, we must reduce the amount of potash added in suitable proportion when nitre is introduced. If 30 parts of nitre per 1,000 of sand are used it is equivalent to $\frac{30 \times 138}{202} = 20.5$ parts of potash, of which $280.8 - 20.5 = 260.3$ parts only are now required. In column 2 will be found the batch containing potassium nitrate.

(137b) **Total Yield and Composition of a Glass from a Particular Batch.**—Example 7.—Consider the soda-lime batch:

Sand	1,000
Soda-ash	370
Limespar	200

The total weight of the materials will be 1,570 parts. Assuming the

materials to be pure, the amounts of the glass-forming oxides obtained from this will be:

Sand, 1,000 × 1	= 1,000 parts	SiO ₂
Soda-ash, 370 × .585	= 216.4	Na ₂ O
Limestone, 200 × .560	= 112	CaO
<hr/>				
Total ..	1,328.4			

The above result has been obtained by multiplying the weights of the batch materials by the factors calculated in the table on p. 138.

The yield will be 1,328.4 parts of glass from 1,570 parts of batch, or $\frac{1328.4 \times 100}{1570} = 84.6$ per cent., the remaining 15.4 per cent. passing away

as gas. In practice, the full yield is never obtained; slight losses of sand or alkali mechanically removed by the draught, or of alkali by volatilisation, or loss by the formation of "gall," are all factors which would reduce the amount of glass obtained. Another source of loss which would be inevitable would be the loss of moisture which would form a part of even the purest constituents. A yield of about 80 to 82 per cent. would be the maximum which could be obtained. On working the glass, further losses would result in the formation of "moils" on the pipe, and in faulty and defective glassware, and in losses in the lehr, so that the percentage yield of finished glassware might be well below 80.

The composition of the 1,328.4 parts of glass obtained is given above in terms of the constituent oxides. If we now consider 100 parts of glass the amounts of the oxides composing it will be:

SiO ₂	$\frac{1000 \times 100}{1328.4} = 75.3$
Na ₂ O	$\frac{216.4 \times 100}{1328.4} = 16.3$
CaO	$\frac{112 \times 100}{1328.4} = 8.4$

The above figures are evidently those of the *percentage* composition of the glass.

Example 8.—Where cullet is added with the batch it remains unchanged in weight in the glass. Taking the above batch with the addition of 500 parts of cullet per 1,000 of sand, the yield of glass will be:

Batch				Glass.			
Sand	1,000 parts.	SiO ₂	1,000 parts.
Na ₂ CO ₃	370 "	Na ₂ O	216.4 "
CaCO ₃	200 "	CaO	112 "
Cullet	500 "	Cullet	500 "
<hr/>				<hr/>			
Total	..	2,070	..	Total	..	1,828.4	..

The percentage yield of glass will be $\frac{100 \times 1828.4}{2070} = 88.3$.

The final composition of the glass is dependent upon the composition

of the cullet. If the latter is of the same composition as the glass obtained from the batch materials alone, addition of cullet in any proportion will cause no change in the relative amounts of the different oxides present in the glass.

Example 9.—We have, so far, considered only the yield and composition of a glass from pure batch materials. Where the substances used are not pure, they must first be analysed before the composition of the resulting glass can be calculated. Take as an example a batch of the following type:

						<i>Parts by Weight</i>
Sand	1,000
Soda-ash	300
Dolomite	200
Sodium nitrate	50
Crystal borax	50
Felspar	100
Total weight						1,700

Consider each material in detail:

SAND.		
<i>Composition.</i>	<i>Percentage.</i>	<i>Amount of Oxides in the Glass.</i>
SiO ₂	99.23	$\frac{99.23}{100} \times 1000 = 992.3$
Al ₂ O ₃	0.59	$\frac{0.59}{100} \times 1000 = 5.9$
Fe ₂ O ₃	0.04	$\frac{0.04}{100} \times 1000 = 0.4$
CaO	0.11	$\frac{0.11}{100} \times 1000 = 1.1$
MgO	0.05	$\frac{0.05}{100} \times 1000 = 0.5$
Loss on ignition	0.18	—

SODA-ASH.		
<i>Composition.</i>	<i>Percentage.</i>	<i>Amount of Oxides in the Glass.</i>
Na ₂ CO ₃	96.08	$\frac{96.08}{100} \times 585 \times 300 = 168.6$
Na ₂ SO ₄	0.56	$\frac{0.56}{100} \times 437 \times 300 = 0.7$
NaCl	0.42	—
Fe ₂ O ₃	0.03	$\frac{0.03}{100} \times 300 = 0.1$
Al ₂ O ₃	0.12	$\frac{0.12}{100} \times 300 = 0.4$
SiO ₂	0.24	$\frac{0.24}{100} \times 300 = 0.7$
Loss on ignition	2.41	—

FELSPAR.

<i>Composition.</i>	<i>Percentage.</i>	<i>Amount of Oxides in the Glass.</i>
SiO ₂	64.44	$\frac{64.44}{100} \times 100 = 64.4$
Al ₂ O ₃	18.75	$\frac{18.75}{100} \times 100 = 18.7$
Fe ₂ O ₃	0.65	$\frac{0.65}{100} \times 100 = 0.6$
CaO	0.27	$\frac{0.27}{100} \times 100 = 0.3$
K ₂ O	13.82	$\frac{13.82}{100} \times 100 = 13.8$
Na ₂ O	2.40	$\frac{2.4}{100} \times 100 = 2.4$

DOLOMITE.

<i>Composition.</i>	<i>Percentage.</i>	<i>Amount of Oxides in the Glass.</i>
CaO	30.51	$\frac{30.51}{100} \times 200 = 61.0$
MgO	20.02	$\frac{20.02}{100} \times 200 = 40.0$
Al ₂ O ₃	1.11	$\frac{1.11}{100} \times 200 = 2.2$
Fe ₂ O ₃	0.81	$\frac{0.81}{100} \times 200 = 1.6$
SiO ₂	0.62	$\frac{0.62}{100} \times 200 = 1.2$
Loss on ignition	46.76	—

BORAX.

<i>Composition.</i>	<i>Percentage.</i>	<i>Amount of Oxides in the Glass.</i>
Na ₂ O	16.2	$\frac{16.2 \times 50}{100} = 8.1$
B ₂ O ₃	36.6	$\frac{36.6}{100} \times 50 = 18.3$
H ₂ O	47.2	—

SODIUM NITRATE.

<i>Composition.</i>	<i>Percentage.</i>	<i>Amount of Oxides in the Glass.</i>
NaNO ₃	97.2	$\frac{97.2 \times 50}{100} \times 0.365 = 17.7 \text{ Na}_2\text{O}$
NaCl	0.4	—
Na ₂ SO ₄	0.6	$\frac{0.6 \times 50}{100} \times 0.437 = 0.13 \text{ Na}_2\text{O}$
Moisture	1.8	—

From the weights of the oxides obtained we may now build up our glass composition:

Oxides Present.	From the—						
	Sand.	Soda-Ash.	Felspar.	Dolomite.	Borax.	Nitre.	Total.
SiO ₂	992.3	0.7	64.4	1.2	—	—	1058.6
Al ₂ O ₃	5.9	0.4	18.7	2.2	—	—	27.2
Fe ₂ O ₃	0.4	0.1	0.6	1.6	—	—	2.7
CaO	1.1	—	0.3	61.0	—	—	62.4
MgO	0.5	—	—	40.0	—	—	40.5
K ₂ O	—	—	13.8	—	—	—	13.8
Na ₂ O	—	169.3	2.4	—	8.1	17.8	197.6
B ₂ O ₃	—	—	—	—	18.3	—	18.3
							1421.1

The percentage yield of glass = $100 \times \frac{1421.1}{1700} = 83.6$. The percentage composition of the glass is:

SiO ₂	$\frac{1058.6 \times 100}{1421.1} = 74.49$
Al ₂ O ₃	$\frac{27.2 \times 100}{1421.1} = 1.91$
Fe ₂ O ₃	$\frac{2.7 \times 100}{1421.1} = 0.19$
CaO	$\frac{62.4 \times 100}{1421.1} = 4.39$
MgO	$\frac{40.5 \times 100}{1421.1} = 2.85$
K ₂ O	$\frac{13.8 \times 100}{1421.1} = 0.97$
Na ₂ O	$\frac{197.6 \times 100}{1421.1} = 13.90$
B ₂ O ₃	$\frac{18.3 \times 100}{1421.1} = 1.29$

CHAPTER XII

THE STORAGE AND MIXING OF BATCH MATERIALS

(138) **The Storage of Batch Materials.**—The day of leaving glass-making materials indiscriminately about yard or factory is passing, for it is now realised how often this results in the collection of impurities. For efficient work a clean, well-arranged batch room in close proximity to the mixing room is desirable. Its position should be decided upon when the factory is first designed, for it must be freely accessible to vehicles, and yet within a short distance of the furnaces it is designed to supply. The room should be kept as dry as possible, since the moisture contents of the materials are otherwise liable to variation, whilst soda-ash, saltcake, etc., tend also to harden into rocky masses. Suitable bins of a size sufficient for the amounts of materials to be stored should be provided, and it is well to locate them, as far as possible, away from outside walls which may become damp.

A modern system, employed by factories consuming large amounts of material, is the use of circular reinforced concrete bins, closed at the top and provided on the flat roof with sliding trap doors. These bins are made to hold several tons of material, according to the requirements of the works, and stand in the open against the rail track by which raw materials enter the works. From the wagons raw material is carried to the top of the bins by an endless belt with conveyer buckets, and then distributed as desired by a horizontal belt or screw conveyers. At the base the bins are hopper shaped, with a central opening closed by hinged doors. On a trackway running under the length of the bins runs a travelling gathering-car which collects the batch as desired, the hinged doors being opened by a lever to allow sufficient material to fall into the car below.

(139) **Batch Mixing.**—After all the ingredients of the batch have been weighed out a thorough mixing is necessary. One of the oldest systems of mixing consists in turning over the batch on a stone, brick, or concrete floor by means of shovels until mixing is judged to be complete. Even in the case of simple batches, when the mixing is of this kind, it is often inefficient, and is the cause of many of the troubles occurring later in the founding process. One particular sample of a batch mixed in this way was found to have a sand content varying in different parts of the mass from 44 to 77 per cent., whilst the limestone content varied similarly from 4·8 to 8·3 per cent. When colouring, and even more particularly, decolourising agents, which form only a small proportion of the total batch, are to be added, the method of hand mixing is extremely likely to give uneven

results. Another great failing of the method is that impurities are likely to be swept into the batch from the floor. In such cases rust and organic impurities are frequently picked up, with prejudicial effect upon the colour of the resulting glass.

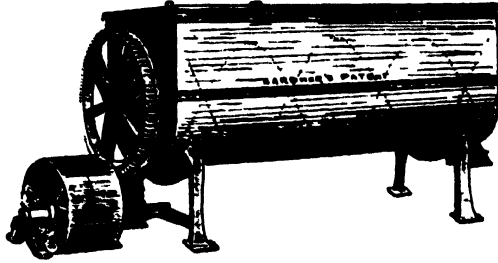


FIG. 26.—A GARDNER MIXER

(By courtesy of Messrs. Wm Gardner and Sons (Gloucester), Ltd., Gloucester.)

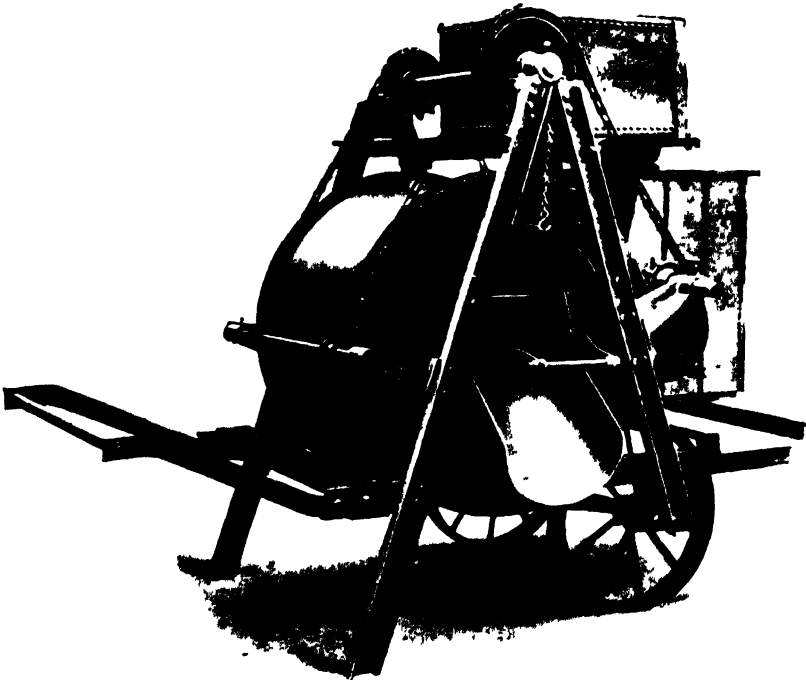


FIG. 27.—THE VICTORIA MIXER.

(By courtesy of Messrs. Stothert and Pitt, Ltd., London.)

A step in advance of floor mixing is hand mixing in troughs, large wooden boxes where the batch can be mixed out of contact with impurities. Here, less foreign matter is likely to invade, whilst in general, the

mixing is likely to be more efficient, the sides of the trough assisting in this respect.

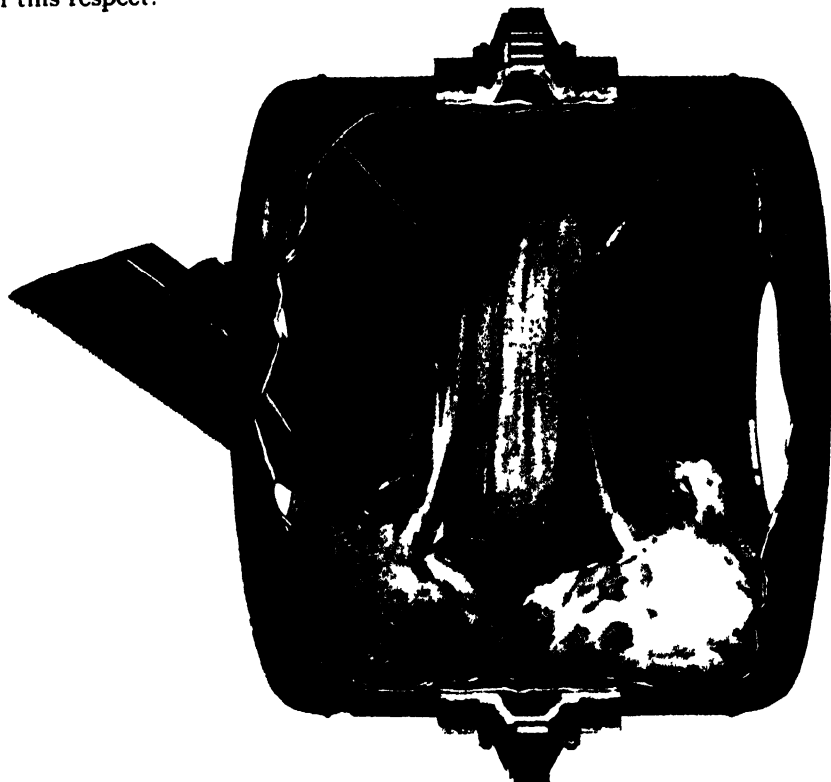


FIG. 28.—THE INTERIOR OF A VICTORIA MIXER.
(By courtesy of Messrs Stothert and Pitt, Ltd., London)

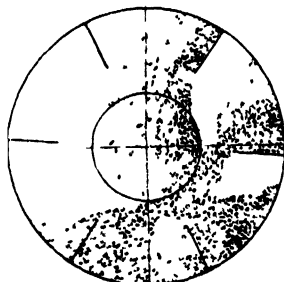


FIG. 29.—DIAGRAMMATIC ARRANGEMENT OF THE RANSOME MIXING WINGS
(By courtesy of the Ransome Machinery Co (1920), Ltd , London.)

(140) **Mixing Machines.**—Mixing machines are now firmly established, and have proved very satisfactory in practice. Two differing types of

machines are employed, the first consisting of a stationary box with rotating blades, the second in which the whole of the mixing chamber revolves.

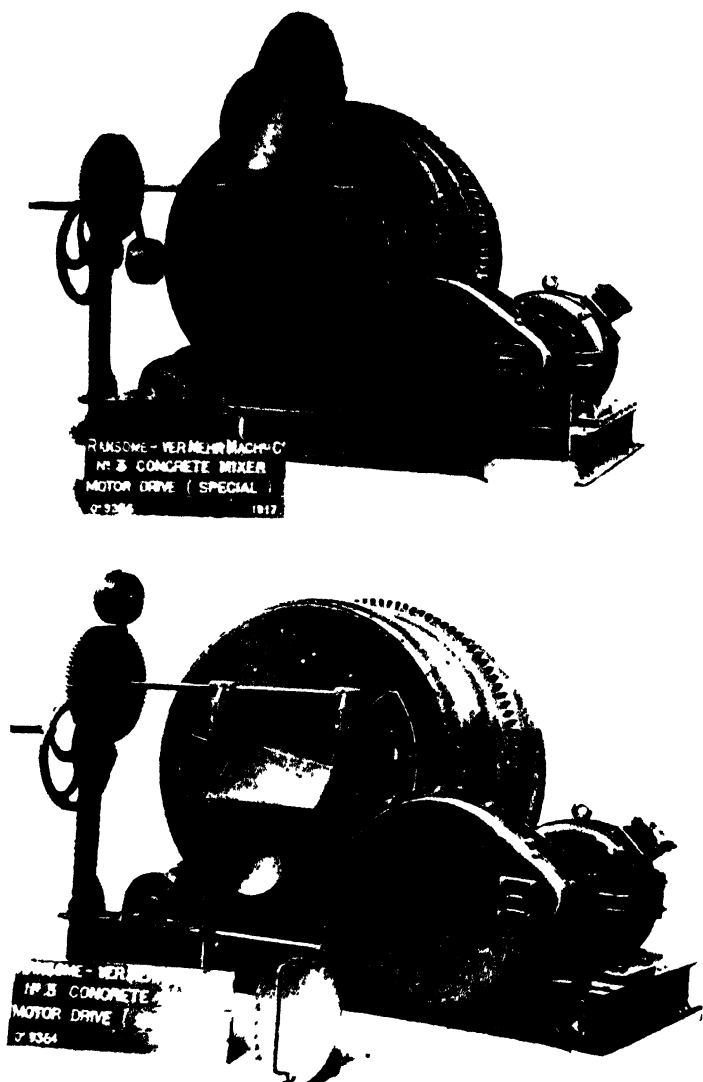


FIG. 30.—THE RANSOME MIXER.

(By courtesy of the Ransome Machinery Co. (1920), Ltd., London)

The *Gardner Mixer* (Fig. 26) is of the former type. It consists of a long iron box with a cylindrical bottom. Through the length of the box passes a power-driven shaft to which are attached two blades so shaped

that they sweep the bottom and prevent aggregation of unmixed portions of the batch. The dotted lines in the illustration indicate approximately the shape of the blades.

In the second class of batch mixers the mixing box consists of a metal drum kept in rotation by means of a toothed rack and provided internally with wings or baffle plates for cascading the batch.

Fig. 27 illustrates a simple portable mixer of this type made by Messrs. Stothert and Pitt, Ltd. The supporting framework is provided with wheels, and allows of batch mixing being performed in any suitable place. A chain drive, hand operated, serves to keep the drum in rotation during

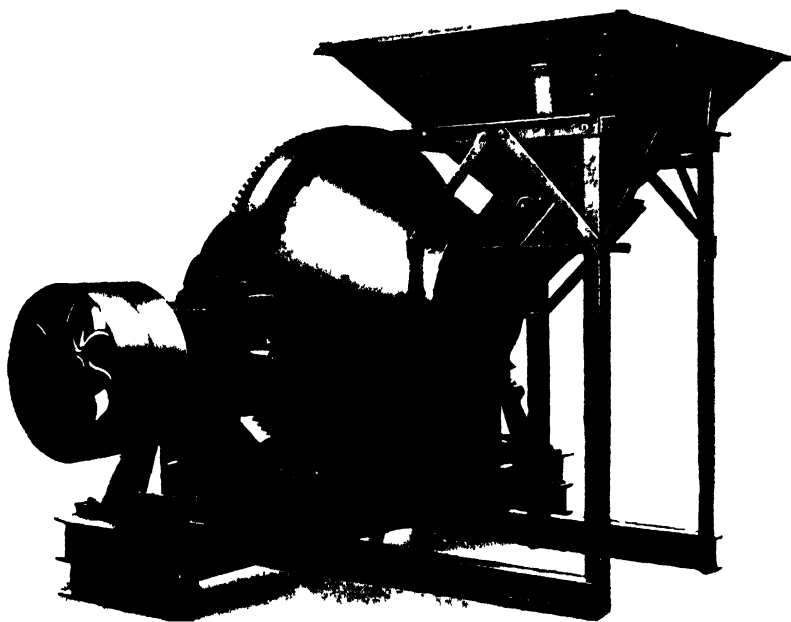


FIG. 31.—THE SMITH MIXER.

(By courtesy of Messrs. Stothert and Pitt, Ltd., London.)

the mixing process Batch materials are fed in through a door at one side of the drum, and are discharged by a second door, provided with a chute at the opposite side. The internal arrangements of the drum are similar to those in Fig. 28, which shows the interior of a power-driven mixer made by the same firm. Four large hopper-shaped blades are fixed so that the batch is constantly poured towards the centre of the drum.

The *Ransome Mixer*, made by the Ransome Machinery Co., is also of the drum type, but operates internally by means of a series of lifting wings and baffle plates (Figs. 29 and 30), by which at each revolu-

tion of the drum all particles of the batch are lifted and turned over, at the same time being intermingled by a transverse oblique action.

The *Smith Mixer*, made by Messrs. Stothert and Pitt, Ltd., is of a somewhat different shape from those previously described (Fig. 31). It consists of a double conical drum with a driving rack placed at the central widest portion of the drum. In this machine the batch is cascaded and mixed by converging mixing blades, as illustrated in Fig. 32.

All the above drum mixers may be supplied with batch hoppers so arranged that when one batch is discharged into the drum a second may be filled into the hopper, so rendering the mixing process continuous.

In many works the mixing machine is placed below the floor level, so that batch materials may be tipped directly down into the hopper without

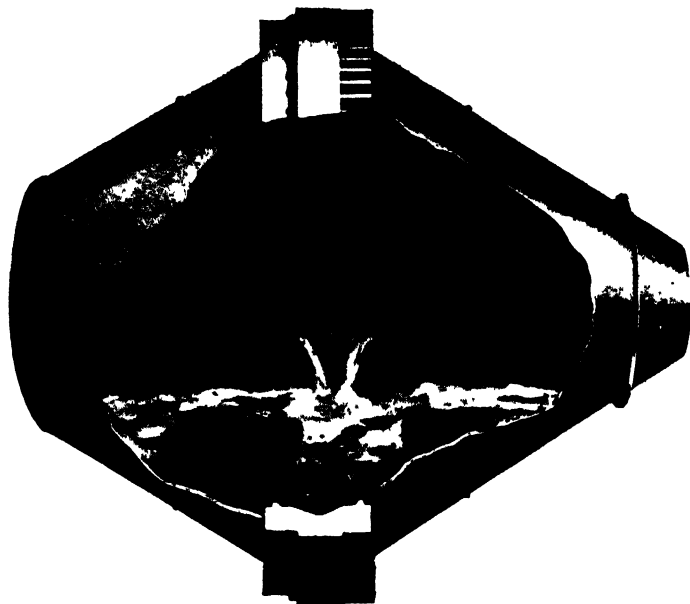


FIG. 32.—THE SMITH MIXING BLADES.

(By courtesy of Messrs. Stothert and Pitt, Ltd., London.)

previously elevating. Where the machine is on or above the floor level special conveyers such as belt-bucket conveyers are necessary for conveying the batch to the hoppers.

A Ransome mixer arranged also as a weighing machine is shown in Fig. 33. This type of machine can gather its own batch materials from the previously described hopper bins, weigh them in so doing, mix them, and finally deliver the well-mixed batch on to a conveyer belt or to a suitable storage chamber.

Addition of cullet is generally performed at the furnace itself, but when this is done it should be closely watched or the relative quantities of cullet and batch will vary greatly. A much better plan is to crush the cullet and weigh it out with batch into the mixer.



FIG 33 —A RANSOME MIXER WITH WEIGHING MACHINE
(By courtesy of the Ransome Machinery Co (1920), Ltd , London)

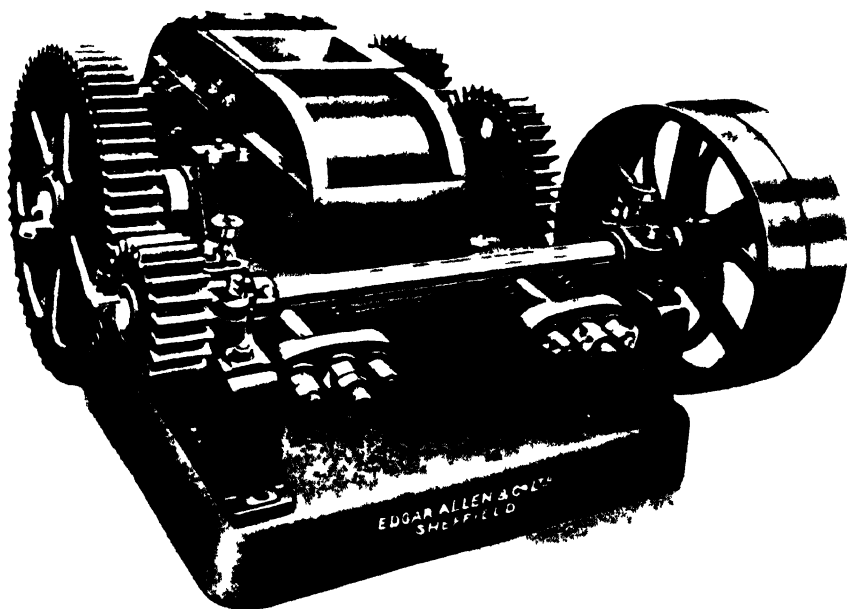


FIG. 34 —EDGAR ALLEN CRUSHING ROLLS
(By courtesy of Messrs. Edgar Allen and Co , Ltd , Sheffield)

Fig. 34 illustrates a simple crushing apparatus suitable for glass, made by Messrs. Edgar Allen and Co. After crushing, it is further advisable to pass the cullet through a magnetic separator, in order to remove iron particles. Where the cullet is actually passed with the batch through the mixer, a mixer of the drum type is essential.

The batch, on its discharge from the mixer, is received in trucks or by a conveyer, and carried to the furnace or to a suitable store. In modern tank practice it is usual to provide a batch hopper above the dog-house

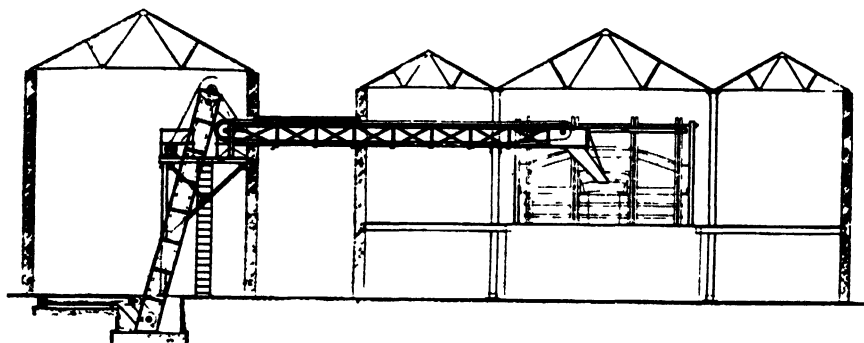


FIG 35.—A BATCH ELEVATOR AND CONVEYER.

(By courtesy of the E. W. Harvey Gas Furnace Co., Ltd., London.)

of the furnace into which the batch is delivered. From this reservoir the batch is allowed to fall into the furnace as desired by the simple operation of a slide (see Fig. 56).

In Fig. 35 will be seen a batch elevator and conveyer as made by the E. W. Harvey Gas Furnace Co., Ltd. The prepared batch is charged on to a small conveyer on the mixing house floor, which takes it to the foot of the bucket elevator; from this it is lifted up to a chute by which the batch is deposited on a strong high level conveyer. The batch is so taken to another chute placed immediately above the small charging tank containing molten glass, into which the batch is dropped and then pushed forward at intervals into the main tank.

CHAPTER XIII

THE COMPOSITION OF GLASS AND DEVITRIFICATION

(141) **The Composition of Glass.**—The nature of glass may be best explained by a consideration of the processes of melting and of cooling from a theoretical standpoint.

MELTING PHENOMENA.—When first the materials composing the glass batch are fed into the furnace they increase in temperature at a rate governed by their heat conductivity and specific heats. As the temperature rises two phenomena are found to occur—namely, the melting of some of the members, and chemical action. Many of the substances used in the formation of glass have definite melting-points as indicated in the following table:

TABLE LVII.—MELTING-POINTS OF GLASS-FORMING SUBSTANCES.

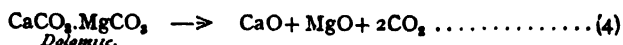
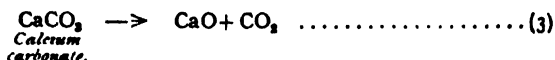
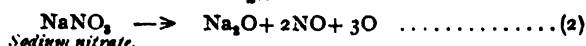
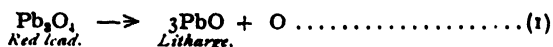
<i>Material</i>	<i>Melting-Point.</i>	<i>Material</i>	<i>Melting-Point</i>
	<i>Degrees C.</i>		<i>Degrees C.</i>
Alumina	2,050	Potassium nitrate	340
Borax (anhydrous)	742	Potash felspar (orthoclase) ..	1,200
China clay .. (approx.)	1,830	Sodium chloride	801
Calcium oxide	2,570	Sodium carbonate	853
Litharge (lead monoxide) ..	880	Sodium sulphate	885
Magnesium oxide (approx.)	2,800	Sodium nitrate	316
Potassium carbonate	885	Soda felspar (albite)	1,100

The above temperatures apply only when the substances are melted alone, and may be greatly affected by the presence of other materials; a good illustration of this being that of a mixture of the two carbonates of sodium and potassium, which, when in equal molecular proportions (*i.e.*, 106 parts of sodium carbonate and 138 parts of the potassium salt), melt at a temperature of 690°, which is much lower than the melting-point of either constituent.

The melting-point of the materials may also be affected by the products of the reactions occurring during the melting process.

At quite low temperatures, and before melting is complete, a number of substances decompose; red lead forms litharge and liberates oxygen, the alkali nitrates yield the oxides, etc., whilst some of the limestone (or

dolomite if this is present) yields the metallic oxide and carbonic acid gas, equations for which actions are as follows:

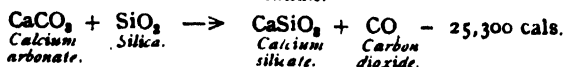
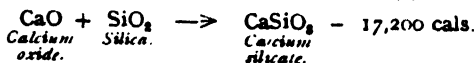


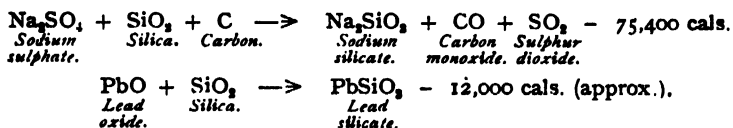
The main reactions upon which the formation of the glass depends are those between the acidic oxides and the basic oxides, carbonates, sulphites or sulphates to produce silicates or borates.

Chemical reactions involve changes of energy between the initial and final states, and, since energy is indestructible, changes of chemical energy are accompanied by equal or opposite changes in some other form of energy, generally of heat energy. In other words, where a system loses a certain amount of chemical energy as the result of a chemical reaction, the energy lost is liberated usually as an equivalent amount of heat energy. When the reaction involves the production of substances possessing a larger total quantity of chemical energy, such reaction can only take place when an equal amount of heat (or other) energy is supplied to the reacting substances—that is, the materials must be heated to cause them to react. The first type of action is said to be *Exothermic*, the second *Endothermic*. An example of an exothermic action is the combination of quicklime with water to give slaked lime, as is evidenced by the fact that the mass increases in temperature. The heat evolution is so large during the process that steam is generally produced, and the mass may even reach 150° C. The amount of heat liberated is quite definite, and is dependent upon the amount of the reacting substances. It may be measured, and it is best expressed in the form of an addition to the chemical equation. The thermal equation for the production of slaked lime from quicklime is:



which means that 56 grams of quicklime unite with 18 grams of water to produce 74 grams of slaked lime, and the reaction results in the evolution of 910 gram calories of heat, sufficient heat to raise the temperature of 100 grams of water by 9.1° C. (from 0° C.). Where the action is endothermic, the fact that heat is absorbed is indicated by a negative sign. The reactions leading to the formation of silicates and borates are endothermic, and the most important ones may be expressed as follows:



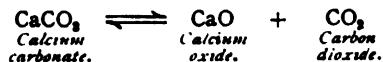


During the period of founding there are thus three definite processes occurring, each of which results in the absorption of heat: (1) raising the temperature of the batch, (2) melting some of the materials, (3) chemical interaction of the constituents. The cumulative effect of the three is strikingly shown in pot furnaces by the fall of temperature inside the pot whilst founding is taking place.

It is well to note here that although heat energy is needed to produce glass from batch materials, it is only a small part of that which is actually obtained in practice from the fuel. Travers* has calculated that a tank furnace, even with efficient working, and producing 1 ton of glass per 0.6 ton of coal used, utilises less than 15 per cent. of the energy derived from the coal in founding the glass, whilst more than five-sixths of the heat is lost outside the furnace or passes away through the furnace walls.

In general, the reactions between the constituents take place more readily when one of these, at least, has melted, molten sodium carbonate, for instance, attacking silica vigorously. It is not essential, however, for melting to have taken place before the reaction commences, and it has been shown that limestone reacts with silica at relatively low temperatures, and when both are in the solid state.† Where substances with low melting-points are present, the so-called fluxes (alkali nitrates, etc.), they may produce a solution of the reacting materials with consequent chemical activity, at a much lower temperature than ordinarily holds, and the founding of the glass is accelerated.

What substances actually are present in the molten glass is difficult to determine, and it will depend entirely upon the conditions of the furnace and the constituents used. That the molten mass consists of mutual solutions of the silicates is probable. It is possible, however, that, at the high temperatures of the furnace, the silicates are wholly or partly broken up into their constituent oxides, a process known as *dissociation*. It is a characteristic of many chemical reactions that they can take place in either direction, the relative amount of the substances present and the temperature governing the direction in which any particular reaction will take place. As an illustration we may instance the decomposition of calcium carbonate by heat into calcium oxide and carbon dioxide.

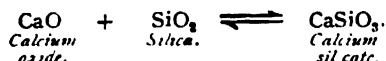


If limestone is heated at a fixed temperature, in a closed vessel, so that the gas produced cannot escape, the concentration of the carbonate will decrease, and that of the decomposition products will increase. With decrease in amount of the limestone the tendency for further

* *J. Soc. Glass Tech.*, 1921, 5, 166.

† J. W. COBB (*J. Soc. Chem. Ind.*, 1910, 29, 253.), states that this action commences at about 800° C.

decomposition will become less, whilst, with increase in the amount of the decomposition products present, they will show an increasing tendency to recombine, until the tendency of the limestone to decompose is just counterbalanced by that of the quicklime and the carbon dioxide to unite, and a state of equilibrium results. At the equilibrium point action and reaction are exactly equal in amount, and the relative quantities of the three substances present remain constant. The equilibrium point is dependent upon the temperature, and increase of temperature serves to cause further decomposition of the limestone until a point is again reached at which the back action is as rapid as the forward one. We may summarise by saying that the heating of limestone in an enclosed space results in the production of an equilibrium in which the relative amounts of the limestone and its decomposition products remain constant, and that the equilibrium point varies with the temperature, the ratio of limestone to quicklime becoming less as the temperature rises. It will be evident that there will be a limiting temperature above which no calcium carbonate can exist at all, for it will be completely dissociated into its constituent oxides. On lowering the temperature below such a point the carbonate again makes its appearance in larger and larger quantities as the temperature falls. Applying the knowledge so obtained to the phenomenon of the combination of the oxide of calcium with silica we obtain the equation regarding the formation of calcium meta-silicate:



In this case none of the constituents are volatile, and it is evidently not necessary to enclose them entirely to secure equilibrium. By analogy it seems extremely probable that with increase of temperature any calcium silicate formed will tend to dissociate into its constituent oxides, and that at very high temperatures it may be completely dissociated, re-forming as the temperature falls.

That free oxides may exist in a solution of silicates is evidenced by the fact that clear glasses, obtained by fusing together sodium carbonate and silica, are only partially soluble in water, and readily devitrify with precipitation of silica when the sodium oxide content is less than 28 per cent., whilst with larger soda contents the glasses are completely soluble and do not deposit silica. A ready explanation is afforded of the phenomenon by the hypothesis that compounds containing less than 28 per cent. of soda are mutual solutions of sodium silicate and silica, whilst beyond this point they consist of solutions of silicates of the types $x\text{Na}_2\text{O} \cdot \gamma\text{SiO}_2$, all of which are soluble in water.

Again, the components of normal glass may vary so much in amount that it is not possible for them to be, in all cases, in strict equivalence for the formation of chemical compounds. This particularly applies when the silica content of the glass is high, for glasses rich in silica fairly easily devitrify with the deposition of the oxide.

We come then to the conclusion that the molten glass consists of the mutual solutions of various silicates (or borates), more or less dissociated into the constituent oxides, according to the temperature of the glass,

together with the excess of the oxides above the amounts which are necessary to produce chemical compounds.

We may note here (Table LVIII) the melting-points of a number of glass-forming silicates, although these again are profoundly influenced by the presence of other substances.

TABLE LVIII.—MELTING-POINT OF SILICATES.

Silicate.				Melting-Point.	Silicate.				Melting-Point.
				Degrees C.					Degrees C
Na ₂ SiO ₃	1,055	BaSi ₂ O ₆	1,426
K ₂ SiO ₃	1,200	Al ₂ SiO ₅	1,816
PbSiO ₃	770	β-CaSiO ₃	1,540

A further modification of calcium silicate, α-CaSiO₃ changes to β-CaSiO₃ at 1300°.

(142) **The Solidification of Glass.**—Let us consider what happens to the molten glass when it is allowed to solidify. We have stated before that solid glass is usually described as an amorphous solid, consisting of a solution of silicates borates, etc., in one another. We must now examine the definition more closely.

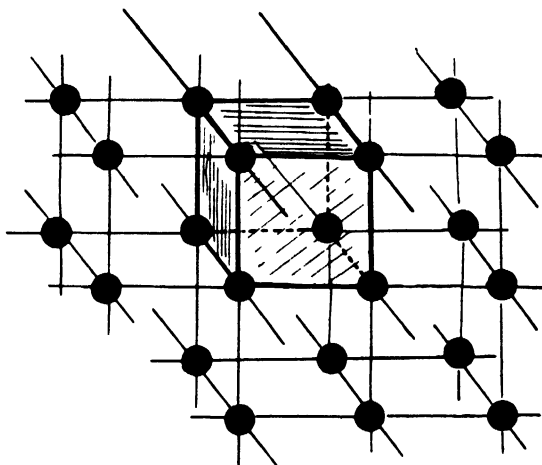


FIG. 36.—CRYSTAL FORMATION

A study of true chemical compounds serves to divide them into two distinct classes: (1) crystalline, and (2) amorphous, of which the former are by far the more numerous. A crystalline substance is one which tends to build itself into a definite shape when the solid is deposited either from the molten state or from a solution. Careful examination of the crystals of a single substance proves them to have bounding faces set at fixed angles to one another, and the substance may be identified by the

angles between the various faces of its crystals. Common salt gives cubical crystals, whilst quartz, as we have seen, forms crystals in which a hexagonal prism is capped by hexagonal pyramids (Fig. 14). It has recently been shown that the crystal is really a magnified picture of the way in which atoms and molecules of a substance bind themselves together when solidification occurs, to produce a perfectly regular lattice-work structure extending in all directions to the boundaries of the crystal. Take a simple case of an element where the atoms are uniformly distributed, and we may obtain the crystal formation indicated in Fig. 36. Here we get a rigid framework with its main planes (those cutting the largest number of atoms) at right angles to one another, and so representing the bounding planes of the substance. The resultant crystalline form is evidently cubic. The simplest form which can be obtained by atoms uniting in this manner is the regular octahedron, and hence it is not surprising to find this form the regular crystalline shape of the elements, carbon, sulphur, gold, lead, silver, etc., all giving octahedral crystals. When two or more differing atoms go to build up the structure, the resultant shape is generally not octahedral or cubical, but some other characteristic shape is assumed, and hence substances may be classified into groups according to their crystalline form. Calcium carbonate crystals are rhombohedral, and the structural arrangements of the atoms (*i.e.*, one of calcium, one of carbon, and three of oxygen) has been worked out.

If, on the other hand, we examine a substance in the molten condition or dissolved in some liquid solvent, we find no such regularity of structure, and in these cases we can only conclude that the molecules are not fixed in position, but are capable of movement throughout the liquid. Let us picture a crystal placed in a liquid containing in solution some of the substance of which the crystal is composed. What happens then is an interchange of molecules between crystal and liquid; the crystal attracts from the liquid, and holds by inter-atomic forces some of the dissolved molecules in its vicinity, whilst other molecules from the crystal surface break away and pass into solution. If more molecules settle upon the crystal surface than break away, crystallisation continues and the crystal grows; but if the reverse holds, and crystals break away faster than they are attracted, the crystal dissolves in the liquid. A high concentration of the solute in the solvent favours crystallisation, as does a low temperature, whilst with low concentration and high temperature solution of the crystal in the liquid is favoured. Considering the case of a crystal in contact with a molten liquid of the same composition, it is the temperature alone which decides whether the liquid will crystallise further or the solid will melt. There is a temperature for each substance at which, in general, it will all crystallise on cooling, and this is called the *freezing-point* of the substance. The freezing-point of water, for instance, under normal conditions is 0°C ., and if a vessel of water is cooled down with stirring, and the temperature observed by means of a thermometer, there will be noted a steady drop until 0°C . is reached, the temperature will then remain constant until all the water is frozen, when it again falls regularly and without further break. The freezing-point of water, or of any crystalline substance, is conveniently shown by plotting a time-

temperature curve—that is, by plotting the temperatures of the water during cooling at frequent and regular intervals of time. Fig. 37 represents a curve of this type for silver, and it will be seen that the curve has a break corresponding to the freezing point of the metal, at which the temperature remained constant over a considerable period of time. The plotting of a time-temperature diagram for a cooling liquid is a common method of determining the freezing-point. For most crystalline substances the freezing-point is perfectly sharp and well defined, the whole of the substance solidifying within a range of less than 1°C . Since, however, freezing depends upon the building up of crystal structure, it is simplified in liquids with a low viscosity, where the molecules can arrange themselves without much friction. Silicates in the molten condition are amongst the most viscous of liquids, and, on cooling, they tend to oppose

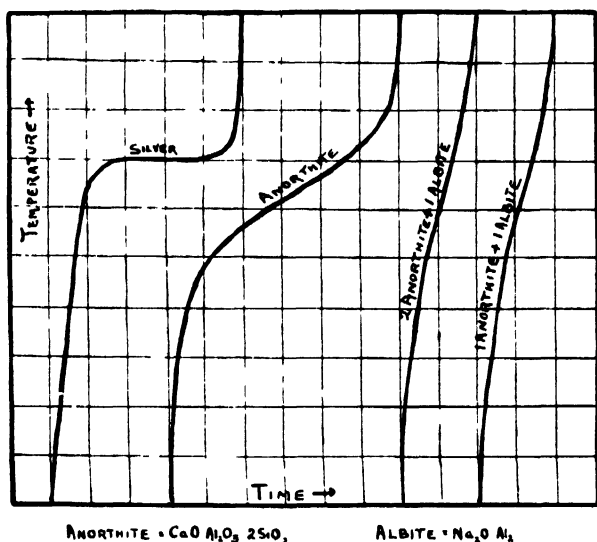


FIG. 37.—FREEZING-POINT CURVES.

crystallisation, so that freezing often extends over a considerable range of temperature, and no well-defined freezing-point occurs. Day and Allen have determined the freezing curves of the feldspars, anorthite and albite, and found the solidifying temperatures to extend over a number of degrees. The curves in Fig. 37 illustrate how ill-defined is the freezing-point of anorthite, and of mixtures of the two feldspars, as strikingly contrasted with the perfectly sharp break in the freezing-point curve for silver; the freezing-point of anorthite extends over a range of 50°C .

When the cooling of amorphous substances is studied, no freezing-point whatever can be found, and the solid has no crystalline structure. Imagine a substance so viscous in the liquid state that the formation of crystals is extremely slow. When the liquid is continuously cooled the viscosity increases until it is so great that the mass becomes rigid, and no movements of the molecules are possible. If the crystals have

not formed before this stage is reached, they cannot then be obtained, so that we have a solid possessing all the configuration of the liquid from which it is formed, and it is distinguished by the term "amorphous." It must be realised that the change from liquid to solid is gradual, and between these states occurs a semi-solid, plastic state, extending below the true freezing-point often by several hundred degrees. Should the substance be kept in the plastic state for any prolonged period crystallisation will set in, and the amorphous structure will be lost. That an amorphous solid is a congealed liquid can be shown in several ways. Many of the physical properties of a crystal vary in different directions through the crystal; thus the conductivity of electricity and of heat, the velocity of light, etc., depend upon the direction in which they are measured relatively to the crystal. In a liquid or an amorphous solid the values of the constants are, in general, the same in whatever directions they are measured. Glass is an example of an amorphous solid or a super-cooled solution. That the substances composing it would crystallise if conditions permitted is shown by the *devitrification* of glass, the formation of dog, etc. In fact, by keeping the glass at a temperature near to the softening point for a sufficiently long period, it is possible to convert the whole of it into a crystalline mass. This requires time even when the glass is soft, and when it is chilled down to normal temperatures the viscosity becomes so great that crystallisation is not possible.

We must conclude that solid glass is much the same in constitution and configuration as the liquid from which it is obtained by chilling, hence we should expect it to be a solidified mutual solution of the silicates, borates, etc., and of the oxides composing these. The fact that many physical properties of glasses are, within close approximation, additive functions might suggest dissociation of the silicates into the oxides, since in the case of solutions of other substances, in which combination can be proved, deviations are generally found from the additive law.

(143) **The Structure of Glass.**—Several methods of attack upon the problem have been suggested.

The first method consists of a study of the behaviour of glass surfaces when subjected to the attack of reagents. From the chapter on "Durability" we see that in the case of soda-lime glasses a fairly resistant member of the series to the attack of reagents is the glass $\text{Na}_2\text{O}, \text{CaO}, 6\text{SiO}_2$. The same glass is also further distinguished by its small tendency towards devitrification, and also by the good results in melting and working.

Zulkowski considers that the initial founding process for the production of glass only results in the formation of simple silicates in mutual solution. The long standing given to the molten liquid in the course of the fining process results in the formation of more complex double silicates, a reaction much slower than the original silicate formation. The simple silicates are fairly easily attacked by chemical reagents, but the complex compounds, so Zulkowski argues, are much more stable towards attack. Hence durability is increased by prolonging the fining period. From a study of the durability of soda-lime glasses this author suggests as a likely complex compound the silicate $\text{Na}_2\text{O} \cdot \text{CaO} \cdot x\text{SiO}_2$,

as being distinctly stable towards the attack of reagents. For complete formation of the double compound the relative numbers of sodium oxide and of calcium oxide molecules present must be equal. If the two oxides do not occur in equi-molecular amount, the glass, when all combination is complete, will be composed of the double silicate, in which is dissolved the rest of the simple silicate in excess. The durability of the glass will then decrease in proportion to the amount of the simple, easily attacked silicate present. Building upon this theory, Zulkowski has attempted to reduce it to a mathematical basis, by comparing the amount of excess silicate with the amount of attack by reagents. In the soda-lime glasses, where the easily dissolved sodium silicate is in excess, it was

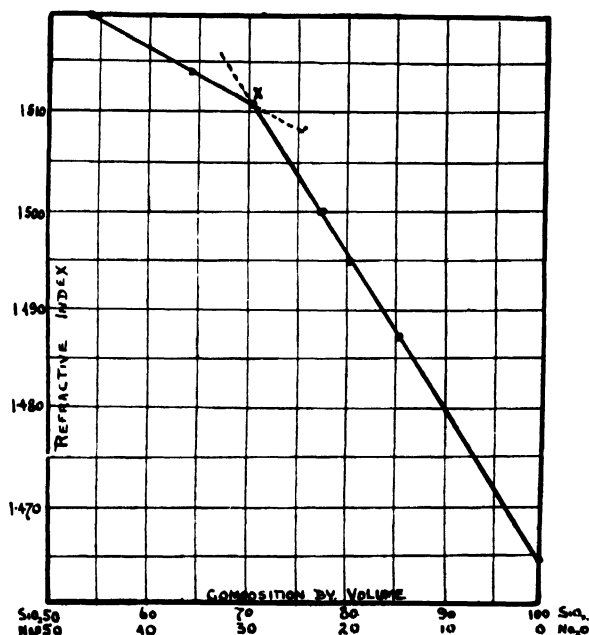


FIG. 38.—TILLOTSON'S REFRACTIVE INDEX-VOLUME COMPOSITION CURVE.

found that the order of increasing divergence from the ratio $\text{Na}_2\text{O} : \text{CaO}$ corresponded with an increasing value of the amount removed by chemical attack. Baillie* has recently enlarged the theory to include such oxides as B_2O_3 , Al_2O_3 , etc., and again finds that the order of stability, as theoretically predicted, varies with the order as found in practice. Ingenious as is Zulkowski's theory, it yet fails to harmonise with a number of the observed properties of glass, particularly with the additive nature of the physical properties.

Another method of attack on the problem has been tried by Tillotson,† who plotted the variation of refractive index, against the variation of composition by volume of the constituents. Theoretical considerations

* *J. Soc. Glass Tech.*, 1922, 6, 68.

† *J. Amer. Cer. Soc.*, 1918, 1, 76.

indicate that where no chemical combination takes place between two constituents, the relationship should be expressed by a straight line. Where a compound is formed the curve will take the form of two straight lines which intersect at a point indicating the composition of the compound. As an example, Fig. 38 is Tillotson's refractive index-volume composition curve for the simple system sodium oxide-silica, and it consists of two lines intersecting at a point corresponding to a compound of the composition $\text{Na}_2\text{O}, 2\text{SiO}_2$. As a further indication of the probability of the existence of such a compound, Tillotson points out that numerous workers have stated that in the glass system sodium oxide-silica, the most acidic mixture of the two, giving a glass completely soluble in water, corresponds to $\text{Na}_2\text{O}, 2\text{SiO}_2$, whilst Gelstharp* stated that of all fusions of sodium carbonate and silica, only those with silica not in excess of the ratio $\text{Na}_2\text{O} : 2\text{SiO}_2$ gave clear solutions containing no undissolved silica, immediately the reaction was complete, as evidenced by the cessation of the evolution of bubbles of carbon dioxide. Against these facts may be placed, however, the following: (a) The points in the refractive index-volume composition diagram would fit a hyperbolic curve almost as well as two straight lines, in which case no compound formation would be predictable; (b) Peddle† found that, in the case of a series of sodium silicate meltings, the glasses with a silica content up to that contained in the compound $\text{Na}_2\text{O}, 2.5\text{SiO}_2$ were practically completely soluble in water.

It is evident that more investigation upon these lines is needed before a final pronouncement can be made. Other compounds claimed to have been proved by Tillotson were $\text{CaMg}_3(\text{SiO}_3)_4$ and $\text{Ca}_4\text{Mg}(\text{SiO}_3)_5$ in the magnesium silicate-calcium silicate melts, $\text{Na}_2\text{O}, \text{BaO}, 3\text{SiO}_2$ and $\text{Na}_2\text{O}, \text{BaO}, 4\text{SiO}_2$ in the sodium silicate-barium silicate glasses, and, finally, the compound $2\text{Na}_2\text{O}, 3\text{CaO}, 7\text{SiO}_2$ in the sodium silicate-calcium silicate series of glasses.

Where matt etching of glass is performed (see Etching), by means of fluoride solutions, crystal figures are obtained, which at one time were thought to indicate crystal structure in the glass. By examination, Tillotson‡ has shown that the shapes are produced by the protective action of crystals formed on the surface of the glass during the etching, and hence that they give no indication of the structure of glass itself.

It will be seen how meagre is the present knowledge of the structure of glass, but another mode of study of the problem, that of the nature of the compounds obtained during devitrification, is of theoretical interest, and also has given results of important practical application.

(144) **Devitrification of Glass.**—Used in its strictest sense, the term "devitrification of glass" indicates the crystallisation of one or more of its constituents. This may occur in the glass when in the molten condition, or even, though at a much slower rate, when the glass is in a plastic, semi-solid condition. The devitrification merely consists in the precipitation from solution of a substance present in greater quantity than can remain dissolved in the liquid. We shall better understand the conditions governing devitrification by first considering the much simpler

* *Trans. Amer. Cer. Soc.*, 1912, **14**, 647. † *J. Soc. Glass Tech.*, 1920, **4**, 14.

‡ *J. Ind. Eng. Chem.*, 1917, **9**, 937.

case of a solution of potassium nitrate in water. The amount of nitre soluble in 100 grams of water varies with the temperature, and is 12 grams at $0^{\circ}\text{C}.$, 22 grams at $25^{\circ}\text{C}.$, 45 grams at $50^{\circ}\text{C}.$, 110 grams at $75^{\circ}\text{C}.$, and 235 grams at $100^{\circ}\text{C}.$ Increase of temperature favours solution, a very general but by no means universal condition, and 20 times as much of the salt can be taken up by boiling water as by water at the freezing-point. Imagine, now, a solution of potassium nitrate to be saturated with the salt at $100^{\circ}\text{C}.$, and then cooled down. It is evident that, as the temperature falls, there will be more solid present than the water can, at lower temperatures, take into solution, and solid will tend to crystallise out, until the saturation point of the liquid is reached. We say *tend*, because it is possible, by cooling the nitre solution carefully, without shaking or disturbing the liquid, to obtain a solution at lower temperatures holding more solid than can actually be caused to dissolve at the temperatures in question; in fact, the whole amount may still remain dissolved, forming what is termed a *super-saturated solution*.

Consider the solution cooled to $50^{\circ}\text{C}.$; at this point there will be more than five times the amount dissolved than will cause saturation. If the super-saturated solution be disturbed, particularly by dropping into it a crystal of nitre, the excess salt will almost instantaneously crystallise out, the effect being startling in its suddenness.

When super-saturation is not allowed to occur, the excess salt will regularly crystallise out as the temperature falls, to dissolve once again on further heating. The two factors influencing crystallisation are evidently (1) the amount of the substance dissolved, and (2) the temperature of the solution. Increase in the amount of salt present or decrease of the temperature both tend to produce saturation of the solution and deposition of the crystals.

(145) **Freezing-Point Curves.**—The curve showing the variation of the freezing-point of a liquid consisting of two or more components with the variation of the relative amounts of the constituents present is known as the "*freezing-point curve*," and is of great value in elucidating the conditions of solution and devitrification. In the case of potassium nitrate, a solution containing 45 grams of the salt in 100 grams of water, or 31 per cent. of the nitrate and 69 per cent. of water, will deposit crystals of nitre when the temperature falls below $50^{\circ}\text{C}.$, and this is evidently the *freezing-point* of a 31 per cent. solution of potassium nitrate in water. A complete freezing-point curve for the system potassium nitrate-water would give the freezing or crystallising points of all solutions from 0.0 per cent. nitre and 100 per cent. water to 100 per cent. nitre and 0.0 per cent. water. A very simple example of a freezing-point diagram is that of potassium iodide in water, as illustrated in Fig. 39. The ordinates represent temperatures and the abscissæ concentrations which range from 100 per cent. water on the extreme left of the diagram to 100 per cent. potassium iodide on the extreme right. Pure water freezes at $0^{\circ}\text{C}.$, a point represented by **A** on the diagram, but if a little potassium iodide is added to the water the freezing-point is lowered, and the depression increases with increase of the salt until over half the solution consists of potassium iodide. At point **E**, however, a sudden change occurs, and further addition of the salt continuously raises the freezing-point,

as shown by line **EB**. **E** represents the lowest temperature at which any solution of potassium iodide and water will normally freeze. Suppose that we commence with a potassium iodide solution under conditions represented by point **C** on the diagram—that is, one in which a solution of 27 grams of potassium iodide in 73 (i.e., $100 - 27$) grams of water is at a temperature of 24°C . At first, as we cool the liquid, no crystallisation will occur, and conditions will change as represented by the line **CD**. When **D** is reached, the conditions for freezing obtain. What happens then is that *pure water* crystallises out as ice, the temperature being -11°C ., and the solution becomes more concentrated in the salt. It is evident, now, that further cooling will not change the condition of the solution along a line represented by **DE**, for the relative amounts of water

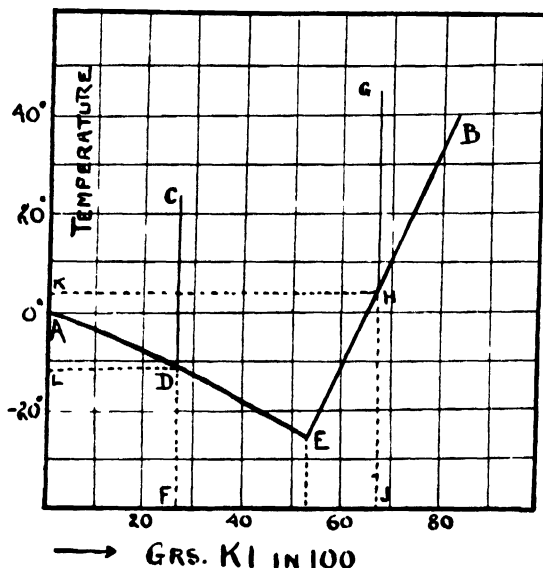


FIG. 39.—THE FREEZING-POINT DIAGRAM OF POTASSIUM IODIDE.

and salt present are changing, as well as the temperature, and what happens is that the composition will change along **DE** until **E** is reached. Here, at about -24°C . and a concentration of 53 grams of potassium iodide per 100 grams of solution (or to 47 grams of water), both water and salt solidify—that is, the solution *crystallises as a whole* without further change of composition and we obtain a solid mass. If, on the other hand, we start at point **G** at a temperature of 45°C . and a concentration of 68 grams of the iodide to 32 grams of water, cooling changes the conditions as represented by **GH** until the freezing-point curve at **H** is reached; then *potassium iodide only* separates out. The composition also changes, and in the direction **HE** until **E** is reached, when again the solution crystallises as a whole. Point **E** is known as the *eutectic point*, and whatever mixture of potassium iodide and water we have, conditions always tend to approach this point when the solution

is cooled, and, when it is reached, the solution completely solidifies before any further lowering of temperature takes place.

The example given is a simple case in which no combination occurs between the solvent and the solute, but when combination between the two is possible the matter becomes more complex. The latter type is well illustrated in the fused system silica-alumina. The two oxides are capable of giving one compound, *sillimanite*, consisting of one molecule of each oxide—i.e., $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, and having the composition 62.9 per cent. Al_2O_3 and 37.1 per cent. SiO_2 . The freezing-point curve is given in Fig. 40. It will be noted that the curve is here composed of two separate sections, $\text{XE}_\text{A}\text{Z}$ and $\text{YE}_\text{B}\text{Z}$, each similar to the simple curve given for

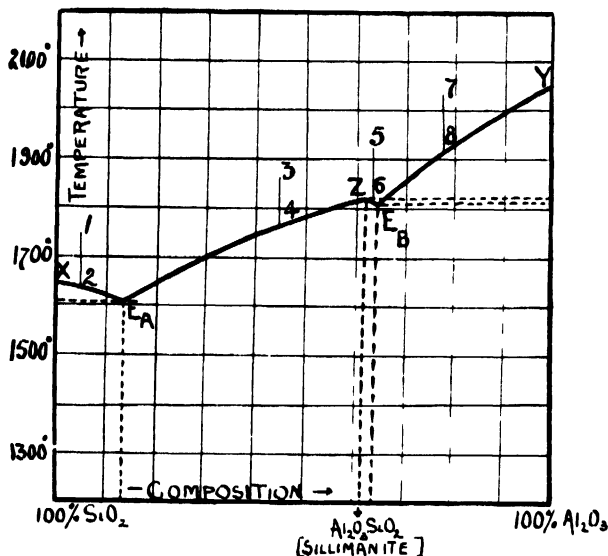


FIG. 40.—THE FREEZING-POINT CURVE OF THE FUSED SYSTEM SILICA-ALUMINA.

the case in which no combination occurs. E_A and E_B are two eutectic points, whilst Z is the point representing the freezing-point of pure *sillimanite*, 1816° C. If we commence at point 1 and cool, crystallisation begins at 2, *cristobalite* (SiO_2) being deposited, and the composition alters until the eutectic E_A is reached, the melt then having the composition 87 per cent. SiO_2 , 13 per cent. Al_2O_3 , when *cristobalite* and *sillimanite* crystallise together and the whole mass solidifies before any further drop in temperature occurs. Eutectic point E_A is at a temperature of 1610° C. If we start at point 3 crystallisation occurs at 4, *sillimanite* being thrown down, until the eutectic E_A is again reached. From point 5, *sillimanite* is deposited when the curve is reached at 6, and the composition alters until the eutectic E_B (Al_2O_3 64 per cent., SiO_2 36 per cent.) is reached, when *sillimanite* and *corundum* (Al_2O_3) crystallise together at the temperature 1810° C. From point 7 cooling causes

precipitation of corundum (Al_2O_3) at 8 until the eutectic E_b is again reached. It must be noted that although *sillimanite* may freeze out along with silica alone at E_a , or alumina alone at E_b , it is impossible for silica and alumina, or *sillimanite*, silica and alumina to crystallise together.

A still more complex curve is that obtained for the fused system silica-calcium oxide. Rankin and Wright* have shown that four different compounds of lime and silica can be obtained—namely, (1) CaO, SiO_2 , *calcium meta-silicate*, (2) $3\text{CaO}, 2\text{SiO}_2$, (3) $2\text{CaO}, \text{SiO}_2$, *calcium ortho-silicate*, and (4) $3\text{CaO}, \text{SiO}_2$, *calcium trisilicate*.

Calcium meta-silicate occurs as the mineral *wollastonite*, stable up to 1200°C. , and as *pseudo-wollastonite*, stable over the range 1200° to 1540°C. , at which temperature it melts. The compound $3\text{CaO}, 2\text{SiO}_2$ breaks up into $2\text{CaO}, \text{SiO}_2$ and melts at temperatures above 1475°C. The trisilicate melts at about 1900°C. and breaks up into $2\text{CaO}, \text{SiO}_2$ and lime. The freezing-point diagram shows three eutectic points, (a) at 1436°C. between silica and calcium meta-silicate, where the mixture has the composition SiO_2 63 per cent., CaO 37 per cent., (b) at 1455°C. between CaO, SiO_2 and $3\text{CaO}, 2\text{SiO}_2$, and (c) at 2065°C. between $2\text{CaO}, \text{SiO}_2$ and calcium oxide. The relative amounts of calcium oxide to silica in glass only allow of the portion of the curve silica-calcium meta-silicate being realised in practice, conditions represented by the curve in Fig. 42. It is evident that above a ratio of 63 per cent. silica to 37 per cent. lime, silica will first crystallise out, whilst between this eutectic point and the pure meta-silicate (51.8 per cent. SiO_2 , 48.2 per cent. CaO) calcium meta-silicate itself will be obtained.

Amongst other systems of importance, from the glass-making point of view, which give eutectics are the following:

System.	Compounds.	Eutectics.	Freezing-Point of Eutectic. (Degrees C.)
Lead oxide-silica ..	PbSiO_3	$\text{PbSiO}_3 + \text{Pb}_2\text{SiO}_4$	690
	Pb_2SiO_4	$\text{Pb}_2\text{SiO}_4 + \text{PbO}$	1170
Lime-alumina ..	$3\text{CaO}, \text{Al}_2\text{O}_3$	$3\text{CaO}, \text{Al}_2\text{O}_3 + 5\text{CaO}, 3\text{Al}_2\text{O}_3$	1,395
	$5\text{CaO}, 3\text{Al}_2\text{O}_3$	$5\text{CaO}, 3\text{Al}_2\text{O}_3 + \text{CaO}, \text{Al}_2\text{O}_3$	1,400
	$\text{CaO}, \text{Al}_2\text{O}_3$	$\text{CaO}, \text{Al}_2\text{O}_3 + 3\text{CaO}, 5\text{Al}_2\text{O}_3$	1,590
	$3\text{CaO}, 5\text{Al}_2\text{O}_3$	$3\text{CaO}, 5\text{Al}_2\text{O}_3 + \text{Al}_2\text{O}_3$	1,700

Simple silicates of definite composition may give freezing-point curves similar to those obtained in the case of the oxides. Wallace† from an examination of the fused mixture lithium meta-silicate ($\text{Li}_2\text{O}, \text{SiO}_2$ or Li_2SiO_3) and sodium meta-silicate (Na_2SiO_3) has discovered a eutectic freezing at 786°C. Sodium silicate and calcium silicate are also stated to give a eutectic freezing at 932°C.

There is another type of freezing-point curve which may be obtained, one in which no chemical compound is formed, but where, when freezing occurs, crystals are deposited *containing both components* in varying proportions. This must be clearly distinguished from the system in

* *Amer. J. Sci.*, 1916, **39**, 1.

† *Trans. Eng. Cer. Soc.*, 1909-10, **9**, 172.

which eutectics occur, for in the latter case single components are first thrown down until the eutectic point is reached, and at this point, although both components are precipitated, the crystals of the two are *quite separate and distinct*. In the case of the precipitation of mixed crystals, however, individual crystals contain both components in such a form as to be indistinguishable, and the crystals are formed at any point on the curve. We may illustrate the mixed crystal type by the freezing-point curve of the metals palladium-gold, given by Ruer,* and reproduced in Fig. 41. It will be seen that the curve is continuous from Pd to Au, the freezing-points of the respective metals. On cooling a fused mixture of the metals, mixed crystals containing both metals in varying proportions separate out, and there is no eutectic point. Wallace has investigated the system sodium meta-silicate (Na_2SiO_3)-barium meta-silicate (BaSiO_3), and obtained, on cooling, an unbroken series of mixed crystals, with no eutectic point and no double silicate.

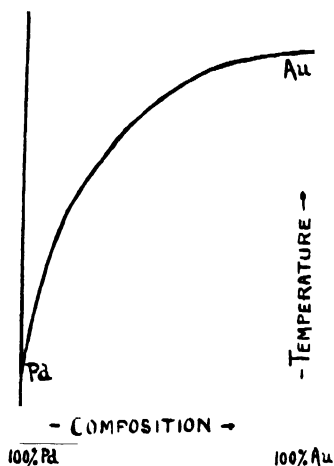


FIG. 41.—THE FREEZING-POINT CURVE OF THE SYSTEM PALLADIUM-GOLD.

Systems of the above kinds of two compounds are termed *binary*, and we have recognised three types: (1) the components do not combine, and are not miscible in the solid state (eutectics are formed); (2) chemical compounds are formed, neither the original components nor the derived substances being miscible in the solid state (eutectics are again obtained); (3) mixed crystals are obtained in the solid state, but no chemical compounds are formed (no eutectics are obtained).

It is possible to have systems combining more than one of the above three types.

Complex as are binary systems, those systems in which three independent components are involved, hence known as *ternary*, are still more complicated. The variations cannot be plotted on two simple rectangular axes, and the freezing-point diagram here takes the form of a

* *Zeitsch. anorg. Chem.*, 1906, 51, 391.

three-dimensional figure. The compositions are indicated by a triangular diagram, as shown in Fig. 2. From each point, a perpendicular is erected and the freezing-point marked off upon it. By joining all the freezing-points so fixed, a model is obtained of triangular plan, and bounded by a number of planes—forming a series of hills and dales. As an indication of the complexity of the problem, we may cite the work of Rankin and Wright* on the system lime-alumina-silica. These workers constructed a ternary model of the type indicated, from which it is possible to predict the separations taking place when any fused mass of lime-alumina-silica is slowly cooled, in what order the separations will take place, and the temperatures at which the various crystallisations will occur. The plotting of the diagram served to show the presence of three new compounds of the composition $\text{CaO}, \text{Al}_2\text{O}_3, 2\text{SiO}_2$, $2\text{CaO}, \text{Al}_2\text{O}_3, \text{SiO}_2$ and $3\text{CaO}, \text{Al}_2\text{O}_3, \text{SiO}_2$, and indicated the melting-points of the compounds.

The model included 30 boundary curves, corresponding to the simpler curves of the binary system, and 14 boundary areas.

Whilst little has been done on the equilibrium of systems giving normal glasses, a number of other similar systems have been examined by various workers. The study by Wallace† of the system sodium oxide-alumina-silica and Ferguson and Merwin‡ of the system lime-magnesia-silica may be mentioned.

It will be realised from the foregoing how complicated is the prediction as to what will be precipitated when devitrification occurs in a system of three components.

At first sight it appears probable that a knowledge of the products of freezing in any system will give an indication of the substances in solution in the cooling liquid. We might predict, for instance, that a fused lime-silica mixture, containing less than 48 per cent. of lime, will contain no free lime, but only a mutual solution of silica and calcium meta-silicate. It would indicate at once, were such an assumption justified, that silicates actually occur in glass, and the amount of these, their composition, and the amounts of the free oxides, in the various glasses, could be obtained by allowing the glass to become completely devitrified and then examining the crystals obtained. Unfortunately the phenomenon of crystallisation is not sufficiently understood for us to say that the substances thrown down are actually present in the solution. Precipitation of the solid may be accompanied by chemical change of which we have no indication. Thus, whilst we can say that it is probable that devitrification does indicate the nature of the solution, we are compelled to wait for further evidence before this fact is established with certainty.

Turning now to the practical application of the facts we have examined, we can form some estimation of what is likely to be precipitated when devitrification occurs in glass. Take the simple system lime-silica, where the silica is present in larger amount than the lime, as is illustrated in Fig. 42. We may first note that, for any concentration of the two constituents, there will be a definite temperature

* *Amer. J. Sci.*, 1916, 39, 1.

† *Trans. Eng. Cer. Soc.*, 1909-10, 9, 172.

‡ *Amer. J. Sci.*, 1919, 48, 81, 165.

above which *no devitrification* can occur, and, with falling temperature, crystallisation only begins when the freezing-point curve is reached. What will be first deposited depends on the relative proportions of lime and silica present, high silica tending to cause precipitation of that oxide, high lime leading to the crystallisation of *wollastonite*. When other oxides are present, as in glass, the case becomes more complicated, and only a complete knowledge of the system will enable us to predict the exact process of devitrification. In general, however, the same two substances as before are liable to be precipitated, silica when present in large quantity, *wollastonite* when the glass is rich in lime. An example has been given of the case of obtaining silica crystals in a glass containing much silica in the manufacture of alabaster glass from a product having

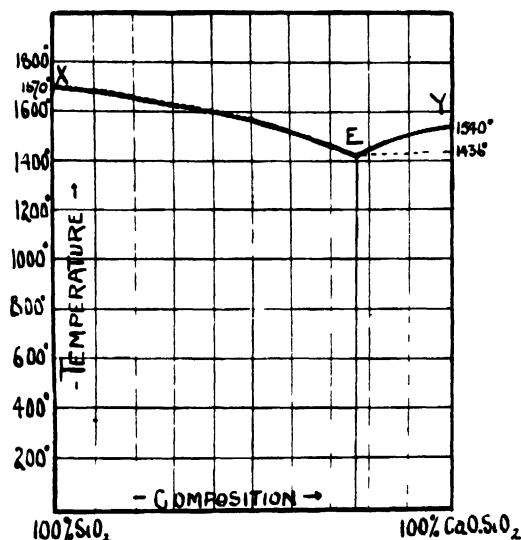


FIG. 42.—THE FREEZING-POINT DIAGRAM OF THE FUSED SYSTEM SILICA-CALCIUM OXIDE.

a silica content approximating to 80 per cent. (see p. 125). Those who use high lime glass for bottles, etc., will also know the ease with which spherical agglomerations of calcium meta-silicate crystals form in the glass. A very common method of getting rid of the crystals, should they appear when the glass is still in the tank or pot, is to raise the temperature above the freezing-point curve, when the crystals will redissolve. Should the temperature again fall to its former level the crystals will again tend to reappear. From an examination of a large number of glasses Peddle* gives the following devitrification limits for various glasses.

(1) Soda-lime-silica glasses tend to devitrify with the precipitation of silica when this exceeds 72 per cent. of the glass. Where more than 10 per cent. of calcium oxide is present, the glass tends to throw down

* *J. Soc. Glass Tech.*, 1921, 4, 34, etc.

calcium silicate if the sodium oxide is more than 20 per cent., but if the sodium oxide falls below 15 per cent., calcium oxide to the extent of 15 per cent. may be added before the glass shows a tendency to devitrification.

(2) Potash-lime-silica glasses have less tendency to devitrify than soda-lime-silicate glasses, there being no separation of silica in any case examined, whilst calcium silicate was precipitated when the potassium oxide exceeded 34 per cent.

(3) Of the sodium oxide-lead oxide-silica glasses examined, there was a tendency to devitrification with deposition of silica when the silica content was greater than 65 per cent., but with the lead oxide content as high as even 55 per cent. there was no tendency to deposit lead silicate.

(4) None of the potash-lead oxide-silica glasses devitrified when treated in the same manner as the analogous soda glasses.

It has been pointed out that, on cooling, all glasses tend to devitrify, but that increase of viscosity hinders the process, until a point is reached at which the viscosity is so great that no separation of crystals can occur.

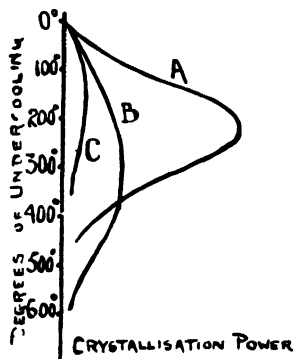


FIG. 43.—BOWEN'S CURVES ILLUSTRATING DEVITRIFICATION.

It is evident that highly viscous glasses will devitrify less easily than less viscous ones. For this reason, lithia glasses, which are less viscous than sodium glasses of similar composition, tend to devitrify more readily than the latter, whilst the soda glasses tend to devitrify more readily than the still more viscous potash glasses. Bowen* has given curves to illustrate the devitrification power of various liquids when under-cooled—i.e., cooled below the freezing-point (Fig. 43). A substance represented by the curve **A** always tends to devitrify rapidly when cooled, whilst **B** tends to devitrify when held for an appreciable time at a temperature even several hundred degrees below the freezing-point; calcium meta-silicate being a case in point.

Curve **C** represents the type of ordinary commercial glasses in which the tendency to devitrification is small. It is evident that glasses are super-saturated solutions, and if reheated to a temperature near to the freezing-point will tend to devitrify. The amount of devitrification will depend upon the time that the glass is kept in the danger zone, and

* *J. Amer. Cer. Soc.*, 1919, 2, 261.

if the period is sufficiently prolonged there may be devitrification even when the glass is several hundred degrees below the freezing-point. The authors possess a portion of a bottle which has remained below a tank furnace for 10 years and is completely devitrified to a white mass, even though the temperature has never been sufficient to soften the glass and cause even the slightest deformation.

There are three periods of danger in founding and working glass, when devitrification may occur. The first is after melting and fining, when the temperature is lowered for working. The glass at this point must not be kept for any length of time below the freezing-out temperature of one of the constituents. When devitrification occurs during this stage, fairly large individual crystals are obtained, since the glass is fairly fluid.

The second period is when the glass is being cooled from the plastic to the solid state. In this case cooling is quicker and smaller crystals result, either evenly distributed or in the form of spheroidal masses, and producing opalescent or milky glasses. It often occurs, where unsuitable glass is used for machines, in the tailings maintained for a considerable period at or near the melting-point. From the point of view of devitrification, a high lime or high silica glass is less suitable for machine work than for hand work, for in the latter case the whole of the glass is rapidly chilled.

The final danger period is when the glass is reheated for after-working. There is a lower limit of temperature of reworking of the softened glass below which it is dangerous to go if devitrification is to be avoided. Bowen found this temperature for certain glasses by heating a piece of devitrified glass at successively higher temperatures for about an hour until the glass became clear. For optical glasses he obtained the temperatures:

<i>Glass.</i>	<i>Temperature of Dis- appearance of Crystals. (Degrees C.)</i>	<i>Composition of Crystals.</i>
Medium flint, $n_D = 1.62$	910	SiO_2
Ordinary crown	1110	SiO_2
Light barium crown	1100	BaSi_2O_5
Light flint	1115	SiO_2

APPENDIX.

Since the foregoing was written on the fused system silica-alumina N. L. Bowen and J. W. Greig* have shown that there is only one compound of alumina and silica stable at high temperatures. This compound, for which the authors propose the name *mullite*, is chemically distinct from sillimanite, $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ since it has the composition $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, but its optical and crystallographic properties are very close to those of sillimanite. On account of this similarity of properties the crystals of the $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ compound have been regarded as sillimanite in earlier work.

* *J. Amer. Cer. Soc.*, 1924, **7**, 238.

CHAPTER XIV

COMBUSTION—THE PART PLAYED BY AIR

(146) **Combustion.**—For the making of glass and for many subsequent operations in the manipulation and fashioning thereof, heat is necessary. This heat is produced in some few cases by means of electricity, but in almost all types of furnaces used in glass melting, in lehrs or annealing ovens and other forms of works appliances where heat is necessary, it is produced by the combustion of substances called *fuels*. It is therefore intended in this chapter to consider the phenomena of combustion, and in subsequent chapters the nature and methods of using fuels.

Combustion is a type of chemical action. When two substances react with one another and chemical combination takes place the action is very frequently accompanied by the evolution of heat. Combustion is said to take place where the heat produced is sufficient to cause the reacting substances, or the products of the reaction, to emit light. The amount of heat produced may be very small, and in this case the combustion is termed incipient or slow, but when a large amount of heat and light is obtained the combustion is termed active or rapid. In the glass industry, where high temperatures, the result of the application of much heat, are required, a rapid form of combustion is desired. Therefore, so far as the industrial furnace is concerned, combustion may be defined as *vigorous chemical action accompanied by the evolution of heat and light*. Two essentials are concerned in the production of heat by combustion—namely, the fuel or combustible substance and air, the supporter of combustion. The function of the latter is sometimes lost sight of, since air in itself has no economic value, but the supply of air and the efficient regulation of this supply are vital factors in the economical utilisation of all forms of fuel for heating purposes.

It is quite well known that the domestic fire will not burn satisfactorily, nor will the industrial furnace work well, without a good draught, whilst, in many cases, gas furnaces are worked with air introduced under pressure. Again, if a lighted candle be placed in a vessel and the air rapidly removed from the vessel by means of an air pump, the candle flame dwindles and is finally extinguished. It is therefore obvious that air, the supporter of combustion, is just as essential as fuel, and since the nature of air is simpler than that of fuels, those properties of air which make it essential to combustion will be considered first.

(147) **The Composition of Air.**—The Swedish chemist, Scheele, came to the conclusion, more than 130 years ago, that the atmosphere was

composed of a mixture of two gases. He found, further, that one of the gases was the supporter of combustion, and was always used up in the burning of a substance; also that the residue did not burn or support combustion, and was far greater in proportion than the supporter of combustion. The names which were, in the course of time, bestowed on the two gases were *oxygen* for the active, and *nitrogen* for the inactive constituent. Both oxygen and nitrogen are chemical elements. It is therefore clear that a furnace would burn more fiercely, and the temperature obtained be higher, if one could employ the active constituent, the oxygen, without dilution with the other gas. For some purposes, mainly on the small scale, as in small gas injector furnaces and blowpipes, oxygen is used occasionally instead of air, resulting in the production of a very high temperature. The cost of production of pure oxygen on the commercial scale does not, however, permit of its general use in furnace operations.

Whilst oxygen and nitrogen are the two main gases in the air, it has been found to contain other gases, as shown in the following statement of the percentage composition of dry air:

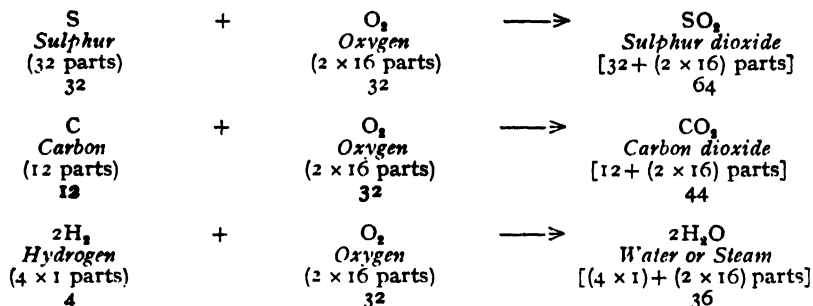
THE APPROXIMATE PERCENTAGE COMPOSITION OF DRY AIR.

	By Volume.	By Weight.
Oxygen	20.99	23.30
Nitrogen	78.03	76.49
Argon	0.95	0.15
Carbon dioxide ..	0.03	0.06
Other inert gases	Traces	Traces

The atmosphere normally contains, in addition to the gases already mentioned, about 1 per cent. of water vapour and traces of hydrogen, ammonia, and nitric acid. Considering air simply as a supporter of combustion it is permissible to neglect the many minor constituents present. So far as combustion is concerned, argon is even more inert than nitrogen, and, grouping the inert gases together, the composition of dry air *by volume* may be taken as approximately:

OXYGEN (<i>active constituent</i>)	21 per cent.
NITROGEN (<i>inactive constituent</i>)	79 "

(148) **The Part Played by Oxygen in Combustion.**—The fact that substances burn in oxygen so much more rapidly and vigorously than in air serves to show that the function of the nitrogen is merely to act as a diluent and render the effect of oxygen less intense. As indicated previously, when combustion takes place a chemical action occurs with combination between the whole or portions of the fuel and the oxygen of the air, producing a compound or compounds of the constituents of the fuel and oxygen. The product of any chemical union of an element with oxygen is, as previously mentioned, called an *oxide*. The following chemical equations illustrate the mode of formation of the oxides of sulphur, carbon, and hydrogen by burning those elements in oxygen:



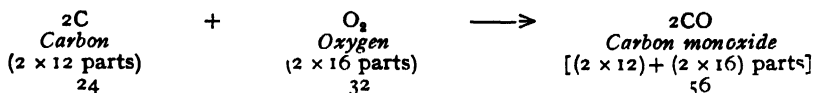
In order to produce rapid combustion the combustible substance must be brought into contact with air or oxygen at, or above, a certain temperature. This temperature is termed the *Ignition Point* of the combustible, and varies with the nature of the combustible and other factors. In order that the combustion may continue, three essentials are necessary: (a) a constant supply of air or oxygen, (b) the maintenance of the substances at or above the ignition temperature, and (c) the removal of the products of combustion. The rate at which combustion will continue depends upon the foregoing three factors, and also upon the area of surface of the combustible exposed to the air or oxygen; the greater the area of surface exposed the greater, in general, will be the rate of burning. Solids, liquids, and gases accordingly differ in their mode of burning. Solids burn best when the pieces are of such a size that they expose the maximum surface area to the accession of air. The largest surface area of any amount of a solid is obtained when the solid is in a powdered form, but if the powder is closely packed the penetration of the mass by air is prevented, or, in any case, strictly limited. If, however, the powdered combustible be used in the form of a spray in the same way as a liquid fuel, it burns very readily.

A liquid normally exposes only its upper surface to the air, and consequently it must burn slowly, but if projected into the air in the form of a very fine spray it will burn extremely readily. Gases offer the maximum surface area of contact to the air, and consequently burn very easily. If a light be applied to a mixture of a gaseous combustible with air, in many cases combustion occurs almost instantaneously. The rate of reaction may be such as to cause a more or less violent explosion. This instantaneous combustion does not always take place, since the relative proportions of combustible and air which will cause such a reaction can only be varied within certain limits. The combustible, or the air, may be present in such excess as to prevent any combustion occurring. It is possible to have a large enough quantity of coal gas in the atmosphere to smell abominably and sufficient carbon monoxide to cause death by poisoning without any explosion occurring on the lighting of a match.

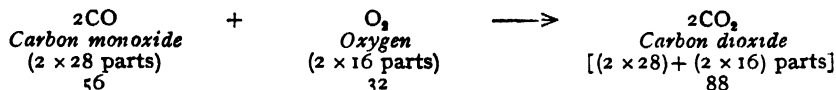
The quantity of oxygen by weight required for the complete combustion of four elementary substances has been stated. If a less amount of oxygen be supplied, the reaction will be incomplete. Combustion is complete, of course, when the whole of the combustible substance is oxidised to its highest state of oxidation. Should the amount of oxygen

be insufficient for complete combustion, then either some of the combustible is left unoxidised or unburnt, or some of it is only partially oxidised and so removed along with the other products of combustion.

Common fuels consist chiefly of carbon and hydrogen. The latter substance can only form one compound on burning—namely, water or steam, and consequently partial oxidation cannot occur in this case. Either the hydrogen is oxidised to water (or steam) or it is untouched. Carbon, however, may form two compounds by union with oxygen. As shown on p. 178, if twelve parts of carbon unite with thirty-two parts of oxygen there are formed forty-four parts of carbon dioxide. Double that amount of carbon may unite, however, with the thirty-two parts of oxygen to form fifty-six parts of *carbon monoxide*, thus:

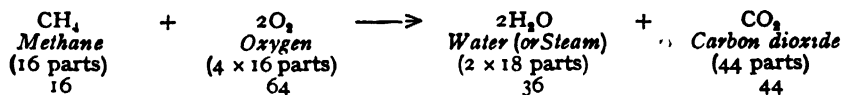


This carbon monoxide may be burned subsequently with a further thirty-two parts of oxygen to produce eighty-eight parts of carbon dioxide as follows:

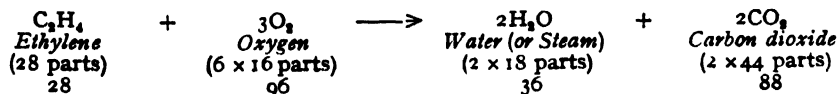


Thus, whether burned completely to carbon dioxide in one or two stages, twelve parts of carbon combine with thirty-two parts of oxygen to form forty-four parts of carbon dioxide.

Fuels do not consist, however, only of mixtures of carbon and hydrogen, but also of compounds of these two elements known as hydrocarbons. About two hundred hydrocarbons are known, and they exist in gaseous, liquid, and solid states. The commonest hydrocarbons encountered in fuel practice are *marsh gas* or *methane*, CH_4 , and *olefiant gas* or *ethylene*, C_2H_4 . Methane is the chief constituent of the Pennsylvanian *natural gas* and of the dangerous *fire-damp* of the coal mines. It burns with oxygen quite readily, giving a slightly luminous flame, but more slowly than hydrogen or carbon monoxide, and the following equation illustrates the change which occurs:



Ethylene is evolved when coal or oil is heated, and forms the main illuminating constituent of coal gas. The luminosity of its flame is some fourteen times that of methane. When ethylene is burned completely the following change takes place:



It can be seen, therefore, that the combustion of hydrocarbons is more complex than that of elementary carbon or hydrogen. When complete combustion of the hydrocarbons takes place water (or steam) and carbon dioxide are produced. If the combustion is incomplete there may be produced simpler hydrocarbons, carbon dioxide, water (or steam), carbon monoxide, hydrogen, and carbon. Where the products of incomplete combustion consist of colourless gases such as carbon monoxide and hydrogen, the only obvious indication of incomplete combustion is a loss of heat, but when carbon is discharged unburnt it indicates the incomplete nature of the burning in the form of *smoke*. Smoke is always the result of imperfect combustion, and may be due to lack of air or to the cooling of the gaseous mixture, and where smoke is produced it is always accompanied by other products of incomplete combustion, and therefore indicates that fuel is being wasted.

Now, though the introduction of a very large excess of air to the fuel may result in incomplete combustion owing to the cooling effect of the air, it is obvious from the equations already quoted that there is a certain minimum quantity of oxygen required for the complete combustion of all fuels. It is possible to calculate the theoretical amount of oxygen or air required for the burning of any amount of any fuel, although in practice some excess of air or oxygen is always necessary. In succeeding pages types of these calculations are given.

(149) Calculations of the Amount of Oxygen required for the Complete Combustion of Fuels.—

(a) WHEN CARBON IS THE ONLY COMBUSTIBLE (*e.g.*, coke).

12 parts of carbon require 32 parts by weight of oxygen,
 \therefore 1 part of carbon requires 2.67 parts by weight of oxygen.

Thus, if **C** represents the percentage of carbon in the fuel, then **Q**, the weight of oxygen required for the complete combustion of unit weight of the fuel, will be given by the following equation:

$$(1) \quad Q = \frac{C \times 2.67}{100}$$

(b) WHEN CARBON AND HYDROGEN ARE THE COMBUSTIBLES (*e.g.*, hydrocarbons).

4 parts of hydrogen require 32 parts by weight of oxygen,
 \therefore 1 part of hydrogen requires 8 parts by weight of oxygen.

If **H** represents the percentage of hydrogen in the fuel, the weight of oxygen required for the complete combustion of the hydrogen in unit weight of the fuel is given by the following formula:

$$\frac{H \times 8}{100},$$

and combining this with equation (1), **Q**, the weight of oxygen required for the complete combustion of unit weight of the fuel is given by the equation:

$$(2) \quad Q = \frac{(C \times 2.67) + (H \times 8)}{100}$$

(c) WHEN THE FUEL CONTAINS CARBON, HYDROGEN, AND OXYGEN.
 If the fuel contains oxygen it is assumed that this oxygen is already com-

bined with hydrogen, and that the amount of hydrogen in the fuel, free to combine with oxygen of the air when the fuel is burnt, is reduced by one-eighth of the amount of oxygen present in the fuel. This reduced amount of hydrogen is known as the *Available Hydrogen* in the fuel. The amount of oxygen, Q , required for complete combustion of unit weight of a fuel containing carbon, hydrogen, and oxygen, is given by the following equation, where O is the percentage of oxygen in the fuel:

$$(3) \quad Q = \frac{(C \times 2.67) + [(H - \frac{1}{8}O) \times 8]}{100}$$

(d) WHEN THE FUEL CONTAINS CARBON, HYDROGEN, OXYGEN, AND SULPHUR.

Sulphur, as shown on p. 178, combines with its own weight of oxygen to form sulphur dioxide. Therefore, if S be the percentage of sulphur in the fuel, Q is given by the equation:

$$(4) \quad Q = \frac{(C \times 2.67) + [(H - \frac{1}{8}O) \times 8] + S}{100}$$

Oxygen forms about 23.3 per cent. by weight of the atmosphere. Accordingly the weight of oxygen required for complete combustion must be multiplied by 100/23.3 or 4.29, in order to give the weight of air required for complete combustion.

The weight of the products of combustion is obtained simply by adding the weights of fuel and air taking place in the reaction.

Though solid and even liquid fuels may be conveniently dealt with by weight, gaseous fuels, gaseous products of combustion, and the air required for the combustion of all fuels are most easily measured by volume. The connection existing between the proportions in which gaseous elements unite by weight and by volume was first demonstrated by Avogadro, whose "*hypothesis*," now recognised as a fundamental principle, may be stated as: "*Equal volumes of all gases or vapours, under the same conditions of temperature and pressure, contain an equal number of molecules.*" Therefore it follows that the ratio between the weights of equal volumes of any two gases will be the same as the ratio between the weights of the single molecules of the gases. *The relative weights of equal volumes of gases or vapours, in terms of the weight of an equal volume of hydrogen as the unit, are termed their specific gravities*, and therefore, by applying Avogadro's hypothesis, *the specific gravity of a gas is the ratio between the weight of a molecule of the gas and a molecule of hydrogen*. The *molecular weight* of a gas is, however, taken as equal to the ratio between the weight of a molecule of the gas and the weight of half a molecule, i.e., one atom, of hydrogen. Accordingly, the number representing the molecular weight of a gas is double the number representing its specific gravity. In Table LIX. are given the specific gravities, atomic weights, and molecular weights of various substances concerned with fuel and combustion.

TABLE LIX.—THE PROPERTIES OF CERTAIN GASES (OR VAPOURS).

<i>Substance.</i>	<i>Specific Gravity.</i>	<i>Atomic Weight.</i>	<i>Molecular Weight.</i>
Hydrogen	1	1	2
Oxygen	16	16	32
Nitrogen	14	14	28
Carbon monoxide	14	—	28
Carbon dioxide	22	—	44
Methane	8	—	16
Ethylene	14	—	28
Steam (at 100° C.)	9	—	18
Carbon	—	12	24

Now the molecular weight of any gas, expressed in grams, occupies under normal conditions of temperature and pressure, 22·4 litres, or, expressed in pounds avoirdupois, occupies 358·5 cubic feet. Table LX shows the volumes occupied by unit weight of various gases and air under normal temperature and pressure, and also of steam at 100° C.

TABLE LX.—THE RELATION BETWEEN THE VOLUME AND WEIGHT OF GASES AND VAPOURS.

<i>Gas or Vapour.</i>	<i>Volume in Litres per Gram</i>	<i>Volume in Cubic Feet per Lb.</i>
Hydrogen	11·20	179·31
Oxygen	0·70	11·21
Nitrogen	0·80	12·81
Carbon monoxide	0·80	12·81
Carbon dioxide	0·51	8·17
Methane	1·40	22·41
Ethylene	0·80	12·81
Steam (at 100° C.)	1·73	27·70
Air	0·777	12·38

Normal temperature is taken as 0° C., whilst *normal pressure* is taken as a barometric pressure of 760 millimetres or 29·92 inches of mercury.

From equations (1) to (4) it is possible, by means of the figures given in Table LX., to express in volumes at normal temperature and pressure the various weights of the gases.

(150) **The Relation of Gases to Temperature and Pressure.**

THE TEMPERATURE RELATION.—At the beginning of the nineteenth century experiments made by Charles, and soon afterwards by Gay Lussac, enabled the following law, known as *Charles's law*, to be established:

Under a constant pressure the volume of a given mass of gas increases by a definite fraction of its volume at 0° C. for each degree rise in temperature.

This law may also be stated in the following form: When a gas is heated and the pressure kept constant, it increases in volume to the same extent whatever gas it may be.

The fractional increase in volume produced in unit volume of a gas on being heated from 0°C. to 1°C. under constant pressure is termed the coefficient of expansion. If Charles's law were absolutely true then all gases would have the same coefficient of expansion. Gases such as carbon dioxide and sulphur dioxide, which are comparatively easily liquefied, have, however, a distinctly higher coefficient of expansion* than such gases as hydrogen, oxygen, nitrogen, and carbon monoxide. The four last-mentioned gases and air have a coefficient of expansion of about 0.00367 or $\frac{1}{273}$, and this figure is used as the coefficient of expansion of all gases for the purpose of all ordinary calculations.

The standard or normal temperature of a gas, as already mentioned, is taken as 0°C. The coefficient of expansion of a gas being 0.00367 or $\frac{1}{273}$

unit volume of a gas at 0°C. becomes $1 + 0.00367$ or $1 + \frac{1}{273}$ volumes at 1°C.

„ „ „ 0°C. „ $1 + 0.00367 \times 2$ „ $1 + \frac{2}{273}$ „ „ 2°C.

and

unit volume of a gas at 0°C. becomes $1 + 0.00367t$ or $1 + \frac{t}{273}$ volumes at $t^{\circ}\text{C.}$

If V_0 is the volume of a gas at 0°C. , and V_t is the volume of the gas, under the same pressure, at $t^{\circ}\text{C.}$, then

$$V_t = V_0 (1 + 0.00367t);$$

or

$$V_t = V_0 \left(1 + \frac{t}{273}\right).$$

Since Charles's law is similarly applicable to a gas on cooling, it follows that

$$V_0 = \frac{V}{1 + 0.00367t} \text{ or } \frac{V_t}{1 + \frac{t}{273}}$$

It is frequently desired to calculate the volume, V_2 , at a temperature t_2 , from the volume V_1 at a temperature t_1 .

Now

$$V_1 = V_0 (1 + 0.00367t_1)$$

and

$$V_2 = V_0 (1 + 0.00367t_2)$$

Therefore

$$\frac{V_2}{V_1} = \frac{V_0(1 + 0.00367t_2)}{V_0(1 + 0.00367t_1)} = \frac{1 + 0.00367t_2}{1 + 0.00367t_1}$$

and

$$V_2 = \frac{V_1 (1 + 0.00367t_2)}{1 + 0.00367t_1}$$

THE PRESSURE RELATION.—The relation between the volume of a gas and the pressure to which it is subjected was discovered by Boyle in the seventeenth century, and *Boyle's law* may be stated thus:

* Coefficient of expansion of carbon dioxide is 0.00369 and of sulphur dioxide, 0.00385.

The volume of a given mass of gas at constant temperature is inversely proportional to its pressure.

Modern investigation has shown that Boyle's law, like Charles's law, is not exactly true, but for all practical purposes it may be regarded as strictly applicable to all gases. If v be the volume of a gas measured at a pressure p , then the volume v_0 , at the standard or normal pressure of 760 millimetres of mercury, is given by the expression—

$$v_0 = \frac{vp}{760}$$

Similarly, the temperature being constant, the volume v_2 of a gas measured at a pressure p_2 may be obtained from its volume v_1 , measured at a pressure p_1 by the equation—

$$v_2 = \frac{v_1 p_1}{p_2}$$

Though the volumes of gases in practice are generally measured at the atmospheric pressure, it may be necessary at times to calculate the volume V_2 of a gas at a temperature t_2 and a pressure p_2 , from the known volume V_1 measured at a temperature t_1 and a pressure p_1 . The volume V_2 is obtained by means of the equation:

$$V_2 = \frac{V_1(1 + 0.00367t_2)}{(1 + 0.00367t_1)p}$$

(151) **Some Typical Calculations.**—The equations given in preceding pages may be used to calculate the approximately theoretical quantities of air or oxygen required for the combustion of various fuels, and also the quantities of the products of combustion so obtained. In the following examples we include calculations using (I.) Coal, (II.) Oil, and (III.) Gas, and giving:

- (a) The weight of oxygen required for complete combustion.
- (b) „ volume „ „ „ „
- (c) „ weight of air „ „ „ „
- (d) „ volume „ „ „ „
- (e) The weight of the products of combustion using air.
- (f) The volume of the gaseous products of combustion at 0° C. and 760 mm. using air.
- (g) The volume of the gaseous products of combustion at 100° C. and 760 mm. using air.
- (h) The volume of the gaseous products of combustion at 1000° C. and 760 mm. using air.

I.—COAL, GIVING THE FOLLOWING ANALYSIS:

Carbon	84.0 per cent.
Hydrogen	5.0 „
Oxygen	4.0 „
Nitrogen	0.5 „
Sulphur	0.6 „
Ash	5.9 „

(a) From equation (4) on p. 181.

$$1 \text{ kilogram requires } \frac{(84 \times 2.67) + \left\{ \left(5 - \frac{4.0}{8} \right) \times 8 \right\} + 1.6}{100} \text{ kilograms of oxygen}$$

$$= 2.62 \text{ kilograms of oxygen.}$$

1 pound similarly requires 2.62 pounds of oxygen.

(b) From Table LX. on p. 182, 2.62 kilograms of oxygen occupy—

$$2.62 \times 1,000 \times 0.70 \text{ litres at } 0^\circ \text{ C.} = 1,834 \text{ litres.}$$

2.62 pounds of oxygen occupy—

$$2.62 \times 11.21 \text{ cubic feet at } 0^\circ \text{ C.} = 29.37 \text{ cubic feet.}$$

(c) (See p. 181.) 2.62 kilograms of oxygen are contained in—

$$2.62 \times 4.29 \text{ kilograms of air} = 11.24 \text{ kilograms.}$$

2.62 pounds of oxygen are similarly equivalent to 11.24 pounds of air.

(d) From Table LX., on p. 182, 11.24 kilograms of air occupy—

$$11.24 \times 1,000 \times 0.777 \text{ litres} = 8,733.5 \text{ litres.}$$

11.24 pounds of air occupy—

$$11.24 \times 12.38 \text{ cubic feet} = 139.2 \text{ cubic feet.}$$

The volume of air can also be obtained by multiplying the volume of oxygen required by $\frac{100}{21}$ or 4.76 thus—

$$1834 \times 4.76 = 8,729.8 \text{ litres}$$

$$29.37 \times 4.76 = 139.8 \text{ cubic feet.}$$

(e) The weight of the products of combustion, using air, is found by adding the weight of fuel used to the weight of air used, and includes that of the ash of the fuel, the gases produced by the burning of the fuel, and the nitrogen of the air.

(f) 1 kilogram of the coal contains 0.84 kilogram of carbon.

Now (from p. 178) 12 grams of carbon unite with 32 grams of oxygen to form 44 grams of carbon dioxide.

Therefore 0.84 kilogram of carbon unites with 2.24 kilograms of oxygen to form 3.08 kilograms of carbon dioxide.

From Table LX. 3.08 kilograms of carbon dioxide occupy—

$$1000 \times 3.08 \times 0.51 \text{ litres at } 0^\circ \text{ C. and } 760 \text{ mm.} = 1,571 \text{ litres.}$$

Similarly, 1 lb. of coal contains 0.84 lb. of carbon and requires 2.24 lbs. of oxygen for combustion, producing 3.08 lbs. of carbon dioxide. 3.08 lbs. of carbon dioxide occupy—

$$3.08 \times 8.17 \text{ cubic feet at } 0^\circ \text{ C. and } 760 \text{ mm.} = 25.16 \text{ cubic feet.}$$

1 kilogram of the coal also contains 0.05 kilogram of hydrogen. Two grams of hydrogen combine with 16 grams of oxygen to form 18 grams

of water; accordingly, 0.05 kilogram of hydrogen will combine with 0.40 kilogram of oxygen to form 0.45 kilogram of water.

Thus the combustion of the hydrogen of the fuel produces 0.45 kilogram of water measured at 0° C.

Similarly, 1 lb. of the coal contains 0.05 lb. of hydrogen, which combines with 0.40 lb. of oxygen to form 0.45 lb. of water.

The sulphur combines with its own weight of oxygen (0.006 kilogram or 0.006 lb.) to form sulphur dioxide, which dissolves in the water and therefore does not affect the volume of the products of combustion.

[The total oxygen used for combustion is therefore $2.24 + 0.36^* + 0.016 = 2.62$ kilograms (or pounds) as calculated before. This weight of oxygen is obtained from 11.24 kilograms (or pounds) of air, leaving therefore $11.24 - 2.62 = 8.62$ kilograms (or pounds) of nitrogen in the products of combustion.

Now, from Table LX. 8.62 kilograms of nitrogen occupy—

$$8.62 \times 1,000 \times 0.8 \text{ litres} = 6,896 \text{ litres at } 0^\circ \text{ C. and } 760 \text{ mm.}$$

Similarly, 8.62 lbs. of nitrogen occupy—

$$8.62 \times 12.81 = 110.4 \text{ cubic feet.}$$

Therefore, at 0° C. and 760 mm. 1 kilogram of the coal, on complete combustion in air, gives 1,571 litres of carbon dioxide and leaves 6,896 litres of nitrogen, a total volume of 8,467 litres.

1 lb. of the coal under the same conditions gives 25.16 cubic feet of carbon dioxide and 110.4 cubic feet of nitrogen, a total volume of 135.56 cubic feet.

(g) At 100° C. 1 kilogram of coal gives (see p. 183):

$$\begin{aligned} & 8,467(1 + 0.00367 \times 100) \text{ litres of gas.} \\ & = 8,467 \times 1.367 \\ & = 11,594 \text{ litres of a mixture of carbon dioxide and nitrogen;} \end{aligned}$$

but 0.45 kilogram of water, also produced, will occupy (see Table LX.) at 100° C. and 760 mm. a volume of $0.45 \times 1,000 \times 1.75 = 787.5$ litres.

Therefore the total volume of the gaseous products of combustion from the complete combustion of 1 kilogram of the coal in air is $11,594 + 787.5 = 12,381.5$ litres. (This neglects the small amount of sulphur dioxide produced on burning the coal.)

Similarly, 1 lb. of coal gives $135.56 \times 1.367 = 185.3$ cubic feet of nitrogen and carbon dioxide and also $0.45 \times 27.7 = 12.47$ cubic feet of steam, a total of 197.77 cubic feet.

(h) At 1,000° C. the volume of the products of combustion, calculated as in (g), will be, from 1 kilogram of the coal,

$$\begin{aligned} & 8,467 \times (1 + 0.00367 \times 1,000) \text{ litres} \\ & = 8,467 \times 4.67 = 39,541 \text{ litres of carbon dioxide and nitrogen.} \end{aligned}$$

* The total oxygen required is 0.40 kilogram, but since the coal contains 0.04 kilogram of oxygen, the amount needed from the atmosphere is 0.36 kilogram.

And also (from p. 183)—

$$\frac{787.5(1 \times 0.00367 \times 1,000)}{1 + 0.00367 \times 100} = \frac{787.5 \times 4.67}{1.367} = 2,690 \text{ litres of steam,}$$

making a total of 42,231 litres.

Similarly, the volume of the products of combustion from 1 lb. of the coal will be—

$$135.56 \times 4.67 = 633.1 \text{ cubic feet of nitrogen and carbon dioxide.}$$

and also $\frac{12.47 \times 4.67}{1.367} = 42.6$ cubic feet of steam,

making a total of 675.7 cubic feet.

II.—OIL, GIVING THE FOLLOWING ANALYSIS:

Carbon	83	per cent.
Hydrogen	12	„
Sulphur	3	„
Ash and other incombustibles	2	„

The calculations may be made as for the coal. If the oil is measured by volume, the calculations may be modified as follows:

(1) When the oil is measured in litres—

1 litre of water weighs 1 kilogram.

The weight of 1 litre of oil is therefore equal to the specific gravity of the oil (compared with that of water as unity) expressed in kilograms.

(2) When the oil is measured in gallons—

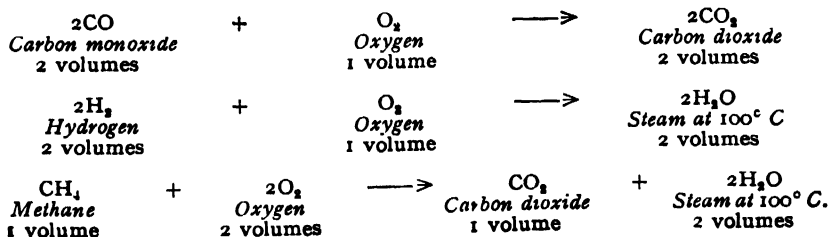
1 gallon of water weighs 10 pounds.

Therefore, if the specific gravity of the oil (compared with that of water as unity) be multiplied by ten the resulting figure expresses the weight in pounds of one gallon of oil.

III.—PRODUCER GAS, GIVING THE FOLLOWING ANALYSIS:

Carbon monoxide	28	per cent. by volume,
Hydrogen	10	„
Methane	4	„
Carbon dioxide	4	„
Nitrogen	54	„

Using gas, we will confine ourselves to volume measurements. The following equations are used for the purpose of these calculations:



(b) Therefore, if 1 litre of the gas be used—

0.28 litre of CO requires $\frac{0.28}{2}$ = 0.14 litre of oxygen for combustion

0.10 „ H₂ „ $\frac{0.10}{2}$ = 0.05 „ „ „

0.04 „ CH₄ „ 0.04 × 2 = 0.08 „ „ „

Thus, 1 litre of the gas requires 0.27 litres of oxygen.

Similarly, 1 cubic foot of the gas requires 0.27 cubic foot of oxygen.

(d) Since 1 litre of the gas requires 0.27 litre of oxygen it will require 0.27 × 4.76 = 1.285 litres of air.

Similarly, 1 cubic foot of the gas will require 1.285 cubic feet of air.

(f) 0.28 litre of CO gives 0.28 litre CO₂.

0.10 „ H₂ „ water.

0.04 „ CH₄ „ 0.04 litre CO₂ and water.

There are also to be taken into account 0.04 litre of carbon dioxide and 0.54 litre of nitrogen from the gas and 1.285 - 0.27 = 1.015 litres of nitrogen from the air used for combustion.

The products of combustion of 1 litre of the gas in air therefore occupy, at 0° C. and 760 mm.:

$$0.28 + 0.04 + 0.04 + 0.54 + 1.015 = 1.915 \text{ litres.}$$

Similarly, the products of combustion of 1 cubic foot of the gas in air occupy 1.915 cubic feet.

(g) 1.915 litres of gas at 0° C. and 760 mm. occupy—

$$1.915 (1 + 0.00367 \times 100) = 2.62 \text{ litres at } 100^\circ \text{ C. and } 760 \text{ mm.}$$

Also, at 100° C., there is 0.10 litre of steam from the hydrogen in the gas, and a further 0.08 litre from the methane. The total volume of the products of combustion at 100° C. and 760 mm. is therefore 2.62 + 0.18 = 2.8 litres.

Similarly, 1 cubic foot of the gas gives 2.8 cubic feet at 100° C. and 760 mm.

(h) At 1000° C. and 760 mm., 2.8 litres measured at 100° C. and 760 mm. occupy—

$$\frac{2.8 \times 4.67}{1.367} = 9.56 \text{ litres.}$$

Similarly, at 1000° the products of combustion of 1 cubic foot of the gas will occupy 9.56 cubic feet.

CHAPTER XV

THE EFFECTS OF, AND THE MEASUREMENT OF HEAT

(152) **The Effects of Heat.**—Certain phenomena of combustion have already been dealt with in Chapter XIV., and in Chapter III. the thermal properties of glass have also been discussed. In this chapter a brief consideration will be given to the general effects of heat and to the methods of measuring heat values.

The effects of heat on a body may be divided into three sections: (1) Rise of temperature; (2) change of size; and (3) change of state.

I.—RISE OF TEMPERATURE.

Temperature is not the same thing as heat. It is simply a condition or state of a body. If a poker be placed in a fire, the end outside the fire quickly becomes too hot to hold. The heat of the fire flows into the poker through the end in contact with it and thence is transmitted along the poker's length, or, in other words, the heat passes from the body at the higher temperature to the one at the lower temperature. Temperature may therefore be defined as the condition that determines which of two bodies, when placed in contact, will part with heat to the other. The body which parts with heat is obviously the one at the higher temperature.

Now heat can be transferred from one place or body to another by three processes; it may be transferred by *conduction*, *convection*, or *radiation*. The poker mentioned above became hot by reason of conduction, the heat being transferred from particle to particle of the poker without causing any visible movement of the poker or of the particles of the material from which the poker was made. Metals generally are good conductors of heat, whilst glass, sand, and stone are bad conductors. Glass tubing may be fused in the blowpipe flame and handled without discomfort to within a short distance of the fused portion owing to its low conductivity. The rate of increase of temperature of a substance depends not only upon the thermal conductivity of the substance, but also upon its specific heat. Consequently the temperature of bodies of the same size and conductivity would rise more or less rapidly according as the specific heats of the substances were small or large. Poor conductors of heat are used as "*heat insulators*," as, for example, the fireclay linings of furnaces or asbestos screens. It is, however, possible to have good conductors of heat used for protection from the effects of high temperature by using them to conduct away heat rapidly in another direction. A typical

example is the Wiegand patent chain screen doors (Fig. 44), which effectively protect workmen from the heat of the furnace when pot setting in the glassworks, and also prevent draughts of cool air from entering the furnace. Similar effects are obtained by the use of wire gauze over the ordinary Bunsen flame. It has already been mentioned that a combustible substance will not burn, even in the presence of air or oxygen, until it is raised to a certain temperature known as the *ignition temperature*. A piece of cold wire gauze, which conducts heat readily, may be pressed down into the Bunsen flame and no flame appears above the gauze, due to the fact that it conducts away the heat from the combustible mixture of gases impinging on it and cools it below the ignition temperature. The application of a flame above the gauze readily kindles



FIG. 44.—THE WIEGAND CHAIN SCREEN.

(By courtesy of the E. J. Codd Company, Baltimore, Md., U.S.A.)

the unburnt gas passing through it. Thus, until the temperature of the wire gauze rises to the ignition temperature of the mixture of gas and air from the burner, no flame appears above the gauze. This phenomenon is made use of in the Davy safety lamp employed in coal mines.

Liquids are generally bad conductors of heat, but mercury and molten metals are good conductors. Gases are even worse conductors of heat than liquids. Liquids and gases are only warmed very slowly when subjected to a heating influence from above, since they are such bad conductors of heat, but if heat is applied from below the portions which are heated first expand, become lighter, and rise. Cooler portions descend to the space previously occupied by the heated part of the fluid, and are in turn heated and rise. There is thus produced, in the liquid

or gas, a rising current carrying heat caused by the movement of the heated particles of the fluid. Currents so produced are termed *convection currents*, and they only occur in liquids and gases where the particles can move freely. *Convection* may therefore be described as the transmission of heat by the actual movement of the particles of a heated fluid. One of the most familiar examples of convection currents is the passage of heated products of combustion from the furnace or fire up the chimney.

The third method by which heat may be transmitted, namely, *radiation*, is quite different from conduction and convection. The conduction



FIG. 45.—REPLACING A HOT POT IN A GLASS FURNACE THROUGH A WIEGAND CHAIN SCREEN.

(By courtesy of the E. J. Codd Company, Baltimore, Md., U.S.A.)

of heat takes place through a body, no matter what its shape may be. Heating by convection always takes place by means of upward currents. A hot body, however, can radiate heat in all directions throughout space, and it does so along straight lines. Since radiant heat travels in straight lines, it is possible to cut off the heat directly radiated from an object by interposing some obstacle between the object and the source of heat. In this way the Wiegand screens, already mentioned, protect the workmen from the tremendous amount of heat radiated from the open furnace. These chain screens, in the form mostly used in glassworks, consist of a multitude of freely hanging individual strands of steel chain sus-

pended close together from a steel bar in a manner to form a continuous sheet or curtain of chain not unlike the familiar Japanese portière. The loosely hanging chains are easily parted and pressed aside by the tools or other objects projected into the furnace, only to fall together again when entrance has been effected. To remove a damaged pot from the furnace the chain screen shield is placed in front of the wall enclosing the pot, the wall is torn down (see Fig. 44), and the hot blocks of which it was composed are dragged through the chain screen and set aside. The absence of heat and glare enables the workmen to operate without discomfort quite near to the opening. Finally, the pot is prised up and removed on the pot carriage. When the truck carrying the new pot reaches the furnace it is pushed boldly through the screen (see Fig. 45). The chains close together, protect the workmen from the radiant heat and the new pot from draughts of cold air, and the work of setting the new pot and walling it in is performed with this transparent shield intervening between the men and the hot furnace. Comfort is assured, and time and money saved during the pot setting operation.

Radiant heat does not sensibly warm the air through which it passes, although some media certainly absorb a portion of the radiated heat passing through them and experience a rise of temperature. This absorption of radiant heat is similar to the absorption of a proportion of light by certain glasses (see p. 36). Whereas heat transference by conduction or convection is a comparatively slow process, radiant heat travels at the same tremendous velocity as light—that is, about 186,500 miles (or 300,000 kilometres) per second. Heat, then, is transmitted by radiation when it passes from one point to another in straight lines, with great velocity and without sensibly heating the medium through which it passes. In the same way as light, radiant heat may be partially reflected on striking an obstacle, partially absorbed by the obstructing medium and partially transmitted through it. Brightly polished surfaces are the best reflectors, and dull black surfaces are the best absorbers of heat, whilst rock salt is perhaps the best example of a solid substance which is transparent to radiant heat. A surface coated with lampblack is capable of absorbing practically all the heat radiation which falls upon it, and such a surface is known as a perfectly black surface.

The atmosphere, when dry, readily allows heat radiation to pass through it, but when the air is damp the water vapour hinders the radiation of heat. Moreover, the radiating power of heated masses of gas varies with the nature of the gas. In glass furnace work, where the heating is obtained very largely by radiation, the presence of a great amount of hydrogen in the gas used as fuel may result in the production of much water vapour, and hence hinder heating by radiation. Accordingly, the presence of more than 18 per cent. of hydrogen in producer gas may decrease the heating efficiency of the gas.

Glass stops radiation from a fire, as is illustrated by the use of glass fire-screens, but where the source of heat is at a much higher temperature than a fire (as, for example, the sun), a considerable amount of the radiant heat is then transmitted by the glass. This is due to the fact that the quality as well as the quantity of the radiation depends upon

the temperature of the source of heat. Glass therefore exercises a selective absorption for heat radiation just as it does for light (see p. 36). As with conduction, radiation depends not only upon the temperature of the hot body, but upon its nature, and particularly upon the character of its surface; the best absorbers, *i.e.*, dull black surfaces, are the best radiators.

II.—CHANGE OF SIZE.

The thermal expansion of glass has already been dealt with in Chapter III., and the effect of heat on the volume of gases in Chapter XIV. Almost all substances expand on heating, but all substances do not expand or contract equally for the same rise or fall of temperature. When furnace bars, bricks, or blocks expand on heating or contract on cooling, they do so to different degrees, and in any case allowance must be made for expansion and contraction. Great force is exerted by an expanding or contracting body, and damage may be done on heating or cooling a furnace if due precautions are not taken for dealing with the change of size.

III.—CHANGE OF STATE.

The application of heat to a body where the rise of temperature is sufficiently great causes a change in the physical state of the body. The change from solid to liquid is termed melting or fusion, whilst the change from solid or liquid to gas or vapour is known as *volatilisation* or *vapourisation*. The temperature at which a substance changes from the solid to the liquid state is known as its melting-point. The reverse change, solidification, takes place at the same temperature, provided the liquid is stirred or shaken as it is cooled.

TABLE LXI.—MELTING-POINTS OF ELEMENTS.

				Degrees C.					Degrees C.
Aluminium	625	Mercury	- 38·5
Bismuth	268	Platinum	1,800
Cadmium	320	Silver	985
Copper	1,096	Sulphur	115
Gold	1,092	Tin	230
Lead	330	Zinc	415

Substances, such as iron, glass, and pitch, become plastic or soften slowly when heated, before they become liquid, and hence they have no definite melting-point. Mixtures and alloys melt at lower temperatures than their constituents. Thus an alloy of bismuth, cadmium, lead, and tin, known as Rose's fusible metal, melts at about 70° C.

When heat is applied to a constantly stirred mixture of ice and water at 0° C. the temperature does not rise until the whole of the ice is melted. This is because the heat applied is being spent in converting the ice to water. The heat so used in producing the change of state—

melting—without change of temperature is called latent heat. In a similar manner, to convert water at 0°C . to ice at 0°C . heat must be abstracted or given out.

TABLE LXII.—LATENT HEATS OF FUSION (IN GRAM CALORIES).

Ice	80.02	Benzene	30.85	Silver	21.07
Sulphur	9.37	Zinc	28.13	Mercury	2.82
Paraffin	35.10	Lead	5.86		

A liquid, or even a solid, may be changed into a vapour in two ways. It may be allowed to stand in the atmosphere to evaporate slowly or to volatilise, or it may be boiled. Water, alcohol, or ether, left in a shallow dish, more or less quickly evaporates, whilst solid naphthalene or camphor will volatilise without first changing to liquid. The distinction between the two processes (evaporation and boiling) is that evaporation goes on at all temperatures, but only from the surface of the liquid or solid, whilst boiling consists of the rapid production of bubbles of vapour throughout the whole bulk of the liquid, and only occurs at a definite temperature known as the boiling-point of the liquid. This temperature is constant for a given liquid as long as the pressure is constant, but as the pressure increases the boiling-point rises, and conversely when the pressure decreases the boiling-point falls.

TABLE LXIII.—BOILING-POINTS.

	Degrees C.		Degrees C.		Degrees C.
Zinc	916	Ethyl alcohol ..	78	Nitrogen	- 196
Sulphur	444.5	Ether	34.6	Hydrogen	- 238
Mercury	357	Carbon dioxide	- 79	Air	- 192
Water	100	Oxygen	- 183		

Heat may be applied to an open vessel containing a boiling liquid without causing any rise of temperature. The heat is expended in converting the liquid to vapour at the same temperature. The quantity of heat which has to be supplied to unit mass of the liquid at the boiling-point to convert it into vapour without changing its temperature, or conversely, the quantity of heat given out by unit mass of the vapour at the boiling-point when condensing to liquid at the same temperature, is called the *latent heat of vapourisation*.

In the melting of glass batches composed of damp materials a considerable quantity of heat is expended in removing the moisture as steam. The greater the quantity of moisture in the batch the greater will be the amount of heat required, and also the time occupied, in raising the temperature of the materials to the point where melting commences.

(152A) **The Measurement of Heat.**—In order to measure heat values it is obviously necessary that some unit or units must be chosen. The unit very commonly used in Britain and America for practical purposes

is the amount of heat required to raise the temperature of one pound of water 1° F. and is known as the *British Thermal Unit (B.T.U.)*. In the metric system the unit is the amount of heat required to raise the temperature of one kilogram of water 1° C. and is termed the *calorie*. For purely scientific purposes the amount of heat required to raise the temperature of one gram of water 1° C. is frequently used as the unit of heat, and is called the *gram-calorie*. The relationship between these units is easily calculated and may be represented thus:

B.T.U.	$\times 0.252$	gives calories.
B.T.U.	$\times 252$	„ gram-calories.
Calories	$\times 3.97$	„ B.T.U.
Calories	$\times 1,000$	„ gram-calories.
Gram-calories	$\times 0.00397$	„ B.T.U.
Gram-calories	$\times 0.001$	„ calories.

The units of heat are referred to water since the amount of heat required to raise the temperature of equal weights of different substances by an equal amount depends upon the nature of the substance and upon its specific heat. Water has a higher specific heat than any other liquid or solid, and its value is taken as unity. Accordingly the specific heat of a substance is more easily defined by comparison with that of water, as in chapter III.

It has already been pointed out in Chapter III. that the specific heat of a substance will not be the same at all temperatures, in fact the specific heats of many substances are greater at low than at high temperatures. Water may be taken as a typical example (see Table LXIV.).

TABLE LXIV.—SPECIFIC HEAT OF WATER

Temperature (Degrees C.).	Specific Heat.
5	1.0041
10	1.0019
15	1.0000
20	0.9987
27	0.9967

The mean specific heat of a substance between any two temperatures T_1 and T_2 is the quantity of heat required to raise the temperature of unit mass of it from T_1 to T_2 divided by the range of temperature $T_2 - T_1$. In the case of gases distinction must be made between the specific heat at constant volume and that at constant pressure. The specific heat of a gas is greater when the gas is heated under a constant pressure (and therefore allowed to expand) than when it is heated at constant volume, and figures for certain gases are given in Table LXV.

The specific heat of a mixture of gases is obtained by multiplying the specific heat of each constituent gas by the percentage of that gas in the mixture and dividing the sum of the products by 100.

The amount of heat required to warm any particular body through a certain range of temperature depends on its specific heat and also on

its mass or weight. The amount of heat which is required to raise the temperature of a body by 1° C. is known as the *Thermal Capacity* of the body, and is the product of the weight of the body and its specific heat.

TABLE LXV.—SPECIFIC HEATS OF GASES (0° C.).

<i>Gas or Vapour.</i>	<i>Constant Volume.</i>	<i>Constant Pressure.*</i>
Air	0·172	0·237
Chlorine	—	0·124
Carbon dioxide	0·173	0·217
Hydrogen	2·402	3·409
Nitrogen	—	0·244
Oxygen	—	0·218

Regnault's figures.

CHAPTER XVI

THERMOCHEMISTRY AND THE VALUATION OF FUELS.

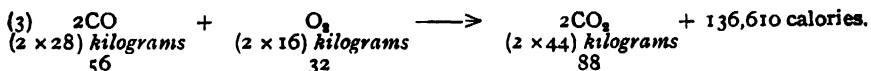
(153) **Thermochemistry.**—It has already been noted in Chapter XIII. that heat may be given out or taken up during the progress of chemical changes. The amount of heat given out or absorbed in any chemical action is quite definite and is entirely independent of any intermediate steps by which the ultimate change may be brought about. Thus, when carbon burns in oxygen or air to form carbon dioxide it gives out heat and any specific quantity of carbon will, on burning, give out a fixed amount of heat. The change may be represented by a thermochemical equation thus:



This equation indicates that 12 kilograms of carbon unite with 32 kilograms of oxygen to form 44 kilograms of carbon dioxide, and in the process give out 97,644 calories. If the carbon is first of all burnt to carbon monoxide, then the equation representing the action is:



When the carbon monoxide is burned to carbon dioxide the following action occurs:

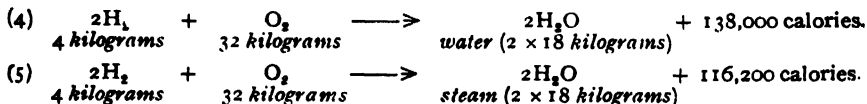


Combining equations (2) and (3) we find that when 24 kilograms of carbon are converted into carbon dioxide by two stages there are evolved $58,678 + 136,610 = 195,288$ calories. One kilogram of carbon accordingly will give out 8,137 calories on burning by the same two stages to carbon dioxide. The same amount of heat given out by one kilogram of carbon is obtained also from the equation (1). Hence, whether carbon is burnt to carbon dioxide in one stage or two stages the amount of heat given out by one kilogram is 8,137 calories. The calorific power of carbon is therefore 8,137 calories.

The heat of combustion of any element may be defined as that amount of heat evolved in producing gram-molecular-volume* of the products of combustion.

* The gram-molecular-volume of a gas is the volume of the molecular weight (expressed in grams) of the gas.

The results of the combustion of hydrogen are represented by equations (4) and (5).



Thus, when the steam is condensed to water at 0°C ., it gives out its sensible heat and latent heat of vapourisation, and the total available heat evolved by the reaction is greater than when the steam remains at 100°C .

Sulphur also gives out heat on burning as represented by the following equation:



From equation (4) it follows that the calorific value of hydrogen is 34,500 calories, and from equation (6) that of sulphur is 2,220 calories.

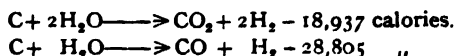
There is a considerable difference between the calorific values of compounds like methane, ethane, and ethylene as obtained by estimation and by calculation from the amounts of the elements present. The reason for this is that when a compound is burned in oxygen or air, the heat evolved is not the same as would be given out by the burning of the same amounts of the constituent elements in the free, elementary condition. The heat obtained from the burning of the compound may be greater or less according as the compound was formed with absorption or evolution of heat. For example, according to equation (1) (p. 197), 12 kilograms of carbon burn to carbon monoxide giving out 97,644 calories. Twenty-eight kilograms of carbon monoxide burn to carbon dioxide, giving out only 68,305 calories, although that amount of carbon monoxide contains 12 kilograms of carbon. Less heat is evolved by the carbon monoxide, since $97,644 - 68,305 = 29,339$ calories of heat are given out during the formation of 28 kilograms of carbon monoxide, as indicated by equation (2), p. 197.

On the other hand, acetylene burns to carbon monoxide and water and gives out heat as indicated in the following equation:



Now 24 kilograms of carbon on burning give out 195,288 calories, 2 kilograms of hydrogen similarly give out 69,000 calories, making a total for the 26 kilograms of 264,288 calories. It is evident that when the 26 kilograms of acetylene were formed from 24 kilograms of carbon and 2 kilograms of hydrogen that $309,200 - 264,288 = 44,912$ calories were absorbed by the reaction.

The reactions which occur in a gas producer between the steam and the incandescent coke are endothermic—*i.e.*, they absorb heat. They may be represented as follows:



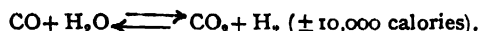
Since the quantity of heat evolved during chemical combination is exactly equal to that requisite to effect the decomposition of the resultant body, it follows that the exact amount of heat required to decompose the steam to hydrogen and oxygen for reaction with carbon is given out again when the hydrogen burns to steam in the furnace.

The reaction represented by the following equation—



is also endothermic. Exothermic reactions tend to take place more readily than endothermic reactions. However, in the reaction in the gas producer just quoted carbon monoxide is formed more rapidly* than it is broken up into carbon and carbon dioxide, and since the carbon monoxide is removed from the system continuously the exothermic reaction rarely occurs. The higher the temperature in the gas producer the greater is the tendency for the endothermic reaction to occur.

Another reversible reaction which may occur in a steam-blown gas producer is represented by the equation:



The reaction producing carbon dioxide and hydrogen is exothermic, whilst the reaction giving carbon monoxide and steam is endothermic. The result obtained will depend on the conditions prevailing; the higher the temperature, the lower will be the percentage of carbon dioxide—that is, the reaction tends to go in the left-hand direction—and excess of steam tends to give a higher carbon dioxide and hydrogen content in the gases.

(154) **The Valuation of Fuels.**—Since fuel is required for the sole purpose of producing heat, its value will depend ultimately on the amount of heat it gives out when burnt—that is, on its *Calorific Power*. The calorific power of a fuel is defined as *the number of units of heat produced by the complete combustion of unit weight of the fuel*. When we say, therefore, that a certain coal has a calorific power of 13,000 B.T.U., we understand that when one pound of that coal is completely burnt, it will produce sufficient heat to raise the temperature of 13,000 pounds of water 1° F. In the United States coal is often purchased on the basis of its calorific power, and the practice is also adopted to some extent in this country, particularly in regard to large contracts delivered over a considerable period of time. As coal represents such a very large proportion of the cost of glass manufacture it is advisable to keep a thorough check on its quality and calorific value to ensure that deliveries are kept up to standard within reasonable limits.

The calorific power of an average sample of each of various solid fuels is given in Table LXVI. on p. 200.

To determine the calorific value of a fuel it is necessary to measure the amount of heat given out during the complete combustion of a known small weight of the fuel. By the use of an instrument known as a calorimeter, in which the heat given out by the combustion of the fuel is

* RHEAD and WHEELER (*Trans. Chem. Soc.*, 1910, p. 2,178) showed that at 850° C. the endothermic reaction proceeded 166 times more rapidly than the exothermic reaction.

caused to heat water, the quantity of heat given out can be found from the weight of water heated and its rise in temperature.

TABLE LXVI.—CALORIFIC VALUES OF CERTAIN FUELS.

<i>Fuel.</i>	<i>Calorific Value.</i>	
	<i>B.T.U.</i>	<i>Calories.</i>
Wood (air-dried)	5,500 to 6,000	1,400 to 1,500
Wood (dry)	7,000 „ 8,000	1,750 „ 2,000
Peat	5,000 „ 8,000	1,250 „ 2,000
Lignite	7,000 „ 10,000	1,750 „ 2,500
Coal (bituminous)	11,500 „ 14,000	2,900 „ 3,500
Anthracite	13,500 „ 14,500	3,400 „ 3,650
Coke	11,500 „ 14,000	2,900 „ 3,500

The calorific power of solid fuels is most accurately determined by burning them in compressed oxygen in a "bomb calorimeter." In calorimeters of this type a known weight of the dry fuel is placed in a capsule or crucible which is supported in the interior of a strong metal vessel. The latter is tightly closed and oxygen is forced into it until the pressure is about 25 atmospheres. The bomb is then immersed in a known weight of water contained in a suitable vessel; the fuel is ignited electrically, and the rise in temperature of the water is noted. The heat given out by the combustion of the fuel is equal to the heat required to raise the temperature of the water and the calorimeter itself through the observed range. For less accurate determinations of the calorific power of solid fuels, many calorimeters have been devised in which the combustion takes place in oxygen at atmospheric pressure. Perhaps the simplest type of calorimeter is that in which the dry powdered fuel is intimately mixed with oxidising agents. When ignited by means of a fuse, the mixture burns without any supply of gaseous oxygen, and the products of combustion bubble through the water in the calorimeter. Determinations of calorific power using this latter type of calorimeter are only approximate, but may be rendered sufficiently accurate for routine works tests. Liquid fuels are usually tested in the bomb calorimeter. For obtaining the calorific power of gases a different form of calorimeter is usually used, although the bomb calorimeter can be utilised.

In the Junkers type of calorimeter as commonly used for gases, the gas is burned at a constant rate and the heat given out is taken up by a constant stream of water flowing through the calorimeter. When the temperature of the water issuing from the calorimeter has become constant, measurements are made during a given short period of time of the volume (*V*) of gas burned, the weight (*W*) of water passed through the calorimeter, and the temperatures of the water on entering (*T*), and on leaving (*T*₁) the calorimeter. The calorific power (*CP*) is given by the equation—

$$CP = \frac{W(T_1 - T)}{V}$$

and is expressed in British thermal units per cubic foot or in calories per cubic metre.

The calorific power of a fuel may also be calculated from its chemical analysis, but calculated values can only be justified when the calorimetric method of estimation cannot be used. The ultimate analysis of a fuel is a laborious process, and should not be undertaken except for some special purpose. It is possible to calculate with fair accuracy the calorific value of coals. A number of formulæ have been suggested by means of which the calorific values of solid and liquid fuels may be determined. The formulæ depend on the assumption that the constituent combustible elements of the fuel burn, each producing its own quantity of heat. The following formula, a modification of that due to Berthelot, is commonly applied to coals:

$$\frac{C \times 8,137 + \left\{ \left(H - \frac{O + N - 1}{8} \right) \times 34,500 \right\} + (S \times 2,220) - (H_2O \times 600)}{100}$$

The letters **C**, **H**, **O**, **N**, **S**, and the formula **H₂O** represent the respective percentages by weight of carbon, hydrogen, oxygen, nitrogen, sulphur and water present in the fuel. It is assumed, for the purpose of calculation, that any oxygen present in the fuel is already combined with hydrogen, and consequently a deduction of one-eighth of the percentage of oxygen from the percentage of hydrogen is made as representing the amount of hydrogen combined with the oxygen. A fixed deduction is made for the nitrogen content of the fuel, and also for the amount of heat assumed necessary for the evaporation of the moisture in the fuel.

When dealing with gases the calorific value cannot be even approximately calculated from the calorific values or heats of combustion of the constituent elements, since gaseous fuels are distinctly exothermic or endothermic. The calorific values of the gases themselves are used, and these are given in Table LXVII.

TABLE LXVII.—CALORIFIC VALUES OF GASES BURNED AT CONSTANT VOLUME.*

	<i>B.T.U. per Cubic Foot.</i>	<i>Calories per Cubic Foot.</i>	<i>Calories per Cubic Metre.</i>
Hydrogen (H ₂) ..	343	86.4	3,051
Carbon monoxide (CO) ..	342	86.2	3,044
Methane (CH ₄) ..	1,063	268.0	9,464
Ethane (C ₂ H ₆) ..	1,852	467.0	16,492
Ethylene (C ₂ H ₄) ..	1,670	421.0	14,868

The effective calorific value of a fuel at a higher temperature is less than that at a lower temperature, since all the products of combustion must be heated up to the same high temperature before any heat is available for further use.

* All at 0° C. and 760 mm.

Another important factor in the economic utilisation of a fuel is the temperature which can be obtained by burning it. This so-called "pyrometric effect" is not the same as the calorific value, nor is it even proportional to it. The temperature attained depends, of course, on the amount of heat liberated by the burning of the fuel; it also depends upon the nature and weight of the products of combustion which take up heat to reach the particular temperature, upon the amount of excess air, upon the specific heats of the products, and upon any heat losses which may occur. It is therefore out of the question to calculate the temperature attainable under practical conditions, but by assuming that the whole of the heat may be utilised without loss it is possible to calculate the maximum theoretical temperature obtainable and so obtain a comparison of the pyrometric value of fuels. This theoretical value is known as the *Calorific Intensity*, and may be defined as the rise of temperature which would result if unit weight of the fuel were burned in the theoretical quantity of oxygen required, the combination being perfect and no heat losses occurring. The fact that the exact variation of the specific heat of gases with increase of temperature is unknown makes even this theoretical value only an approximation to the truth. The temperature could not, of course, be attained in practice. However, an equilibrium is obtained—that is, the heat production becomes balanced by the heat losses. By increasing the draught through a fire, no increase of calorific power can be attained, but the production of heat is more rapid. Since the heat losses do not increase in proportion, a rise of temperature results. If, however, an excessive amount of air be used, the temperature attainable will be substantially decreased. Recuperation or regeneration adds considerably to the calorific intensity obtainable in practice, particularly in the case of poor fuels such as producer gas, and the value of such fuels almost entirely depends on the increase of calorific intensity brought about by preliminary heating before use in the furnace.

Assuming that several samples of coal are equally suitable as regards their properties in the furnace (that is, they burn with comparative ease, burn freely with a long flame or short flame as may be necessary to meet the needs of the particular type of furnace), in order to judge which coal would be the most economical in use it is necessary to consider the following points: first, the price delivered at the works, including cost of carriage; secondly, the quantity of moisture in the coal; thirdly, the quantity and character of the ash left after burning, and particularly its liability to form a fusible clinker; fourthly, the calorific power of the fuel; fifthly, the calorific intensity of the fuel; and sixthly, the possibility of regular supplies.

The economic value of a fuel is measured by the number of heat units available for use per unit of cost. As regards solid fuels it is necessary to determine the moisture, ash, sulphur, coke and volatile matter. Moisture reduces the heating value of the fuel quite apart from the fact that water may be paid for as coal. The ash that is left after the coal is burned is of great importance, both as regards its nature and its amount. In amount, it should be as low as possible, since it is paid for as coal, and not only has it no heating value, but it may have to be removed from the fires whilst still hot

(causing a loss of heat) and then carted away—a further expense. The nature of the ash is also very important. If infusible and powdery, it will fall through the grate of furnace or producer to a large extent, but if fusible it may form hard clinkers on the bars and sides of the grates. The periodical removal of these clinkers entails a lot of very severe work on the firemen, and during the operation it is not only impossible to avoid withdrawing a considerable amount of red-hot coke with the clinkers, but a large amount of cold air is admitted into the fires, cooling them down considerably and causing a serious loss of heat. This process may also cause the serious cracking of pots in a pot furnace through the sudden admission of cold air.

With liquid fuels the important factors are specific gravity, flash-point, water content and viscosity. The ordinary methods of gas analysis may be applied to gaseous fuels.

There are two matters which are exceedingly important in connection with the determination of the heating value of fuels. The first is the question of sampling. In order that a sample of fuel may be entirely representative of the bulk, the taking of the sample must be made by certain fairly well-established methods, and by an experienced sampler. The second question is the determination of the calorific value. The calorific value of fuels can only be accurately determined by means of an up-to-date calorimeter in the hands of a skilled operator. Estimations by an inexperienced person using a simple form of calorimeter can only result in trouble and annoyance, particularly if the values so obtained are used to determine the economic value of a consignment of fuel as between consumer and supplier.

The efficient utilisation of fuels in the furnace can be controlled to a certain extent by the occasional analysis of the flue gases, together with regular determinations of the amount of carbon dioxide in the gases either by some form of gas-analysis apparatus or by the use of a carbon dioxide recorder.

The methods for analysis of fuels, etc., cannot be dealt with in the space available in a book of this character, and those interested are referred to the various authoritative books dealing with the examination of fuels.

CHAPTER XVII

PYROMETRY

(155) **General.**—It is only comparatively recently that the necessity for careful measurement and systematic regulation of high temperatures involved in many manufacturing processes has been recognised. Whilst the metallurgical industries are fairly well equipped in this direction, it must be stated that in the glass industry the estimation and regulation of furnace and lehr temperatures depend very largely upon the experience of the workmen particularly concerned. There is no doubt whatever that an experienced observer is a better judge of the temperature of a furnace than an incorrectly calibrated, or improperly used, pyrometer. However, pyrometers can now be obtained and maintained in such a condition that they give readings of temperatures very much more accurate than any which can be obtained by the unaided human eye.

Now that automatic and semi-automatic machines and feeding devices are coming largely into use in the industry, it is essential that the glass from the furnace shall be of a definite viscosity. A rise or fall in temperature of 50° C. may make all the difference between a correct and an incorrect viscosity—that is, between success and failure in working—and no man can be relied upon at all times to estimate temperatures to within 50° C. The estimate by eye will vary with the physical condition of the man and with the change in surrounding conditions, as from bright sunlight to dull light, and from darkness to artificial light. Accordingly, accurate pyrometric records become invaluable. Again, in annealing, correct adjustment and regulation of lehr temperatures results in a minimum breakage of ware, a minimum length of lehr, and a minimum length of time the ware needs to remain in the lehr. Judgment of the extent of annealing by the “sulphuring” of the ware or the fact that a couple of articles occasionally come down the lehr stuck together is very hazardous and too uncertain in these days of high rate of production and keen competition.

Careful regulation of producer, gas-line and flue temperatures may mean a tremendous saving in the expenditure of fuel. In fact, the better the regulation of the temperatures throughout glassworks operations the lower will be the cost of production, and well-used pyrometers quickly *pay for themselves*.

(156) **Types of Temperature Measuring Instruments.**—Six types of temperature measuring instruments are in more or less common use—namely, expansion, fusion, electrical resistance, thermo-electric, radiation

and optical. Each of these types has its own general characteristics of action.

(157) **The Expansion Type.**—The measurement of temperature by an instrument of this type depends upon the change in length or volume of a body when subjected to changes of temperature. The ordinary mercury thermometer, the gas thermometer, the spirit thermometer, and the tin thermometer are all of this type, and also those depending upon the unequal expansion of metal rods and the contraction of porcelain on heating. So far as high temperature work is concerned the most important of these are the gas thermometer and the tin thermometer.

THE GAS THERMOMETER AND STANDARD TEMPERATURES.—Lord Kelvin in the middle of the last century showed, by his thermodynamical researches, that it was possible to establish a temperature scale independent of the physical or chemical properties of any particular substance but identical with the scale obtained from the expansion of a "perfect" gas. A *perfect* gas is one which conforms exactly to Boyle's and Charles's laws (see p. 183), or, in other words, one in which the expansion, whether under constant volume or constant pressure, is directly proportional to the amount of heat required to produce that expansion. No known gas behaves as a perfect gas, but hydrogen and nitrogen, commonly used in the gas thermometer, do not depart markedly from the conditions specified, and, in any case, the corrections necessary can be calculated.

The gas thermometer of the *constant volume* type consists essentially of two parts, the bulb containing the gas and the manometer used to measure the pressure to which the gas is exposed at the different temperatures. The bulb is made of a substance capable of withstanding the particular temperature used without deformation. Chappuis* used a platinum-iridium alloy bulb with hydrogen, Callendar† used hard glass with air, and Day and Sosman‡ a platinum-rhodium alloy bulb with nitrogen.

The pressure of a gas at constant volume varies directly as the absolute temperature. The absolute zero being taken as -273.13°C. , then if p is the pressure of the gas when the bulb is in melting ice and p_1 the pressure of the gas when the bulb is in steam or subjected to any other temperature, then the absolute temperature, T , of the gas is given by the expression

$$T = \frac{273.13 (p_1 - p)}{p}.$$

By deducting 273.13 from the absolute temperature the temperature in degrees centigrade is obtained.

The gas thermometer is never used for determinations of temperature in the works, since so many adjustments are necessary, and the gas thermometer is a most fragile and cumbersome physical instrument. A thermo-element (see later) is standardised against the gas thermometer, and this thermo-element is used for the determination of certain *fixed*

* *Travaux et Mémoires du Bureau International des Poids et Mesures*, 1888, 6.

† *Phil. Trans.*, 1887.

‡ *Amer. J. Sci.*, 1910, 20, 93; reprint 157, *Carnegie Inst. of Washington*, 1911.

points. In Table LXVIII. are given certain fixed points* according to latest determinations.

TABLE LXVIII.—PYROMETRIC FIXED POINTS.

Fixed Points.						Temperature
						Degrees C.
The freezing-point of tin	231.8
" " " " cadmium	320.9
" " " " zinc	419.4
" boiling " " sulphur	444.6
" freezing " " antimony	630.0
" " " " aluminium	658.7
" " " " sodium chloride	801.0
" " " " silver	960.5
" " " " gold	1063.0
" " " " copper (free from oxide)	1083.0
" melting " " palladium	1555.0

Following the standardisation of the thermoelement the pyrometer to be calibrated may be compared with the thermoelement under suitable conditions.

THE TIN THERMOMETER.—Taking advantage of the properties of tin, which is molten over a range of about 2000° C., increases in resistivity with rise of temperature when in the molten state, increases in volume in a strictly linear manner with rise of temperature, does not form a carbide in the presence of graphite and maintains its purity in an atmosphere of carbon monoxide at the highest temperature at which it is molten, Northrup† has developed a "tin pyrometer." Constructed on the general lines of a very large mercury thermometer, it depends for its indications on the linear expansion of tin.

The bulb (Fig. 46) is made of close-grained graphite, and as the temperature of the tin rises above 700° C., the tin expands into the graphite stem. The height of the column of tin is determined by the establishment of electrical contact through a nickel wire. The scale is fixed upon by calibration at certain fixed points, and extended in the higher temperature region on the assumption that the expansion of the tin continues to be linear. The limit of usage is known to be above 1680° C., and is thought to be above 1800° C. The bulb and stem may be protected from oxidation by being enclosed in a carborundum (refrax, silfrax or carbofrax) tube, and immediately surrounded by molten tin.

This type of pyrometer is for direct insertion into furnaces or kilns, and is only intended for permanent installation in a furnace of comparatively large dimensions. It does not register a "point" temperature as a thermocouple does, but the mean temperature over the space occupied by the pyrometer bulb, and must be maintained approximately in a vertical position. Northrup advocates consideration for this pyrometer

* W. E. FORSYTHE, *J. Opt. Soc. Amer.*, 1920, 4, 305.

† *Trans. Faraday Soc.*, 1917-18, 13, 212.

as a possible means of extending the fundamental temperature scale above 1555°C. , the present limit of the gas thermometer.

(158) **The Fusion Type.**—We may mention under this heading Seger cones (see p. 289 for details), Watkin's heat recorders, and the system of fusible alloys.

The recorder devised by H. Watkin* in 1899 consisted of a block of refractory ware with five circular recesses sunk in its top face. In these recesses were placed pellets of fusible materials of definite composition and melting-point. After firing, those pellets which have been fused remain in the recesses and give a record of the highest temperature reached. These recorders give no indication, of course, of the length of time the particular temperature has been maintained.

Thin sheets of metals or alloys have been used in Germany for determining temperature. The metals used were silver, gold, and platinum, and alloys of silver and copper, silver and gold, and gold and platinum. The gold-platinum alloys registered temperatures, according to their composition and fusion-point, varying from 1100°C. to 1385°C. , but the disadvantage attaching to their use is their slow rate of fusion.

(159) **The Electrical Resistance Type.**—Sir William Siemens in 1871 suggested that the change in electrical resistance of a wire with temperature might be employed as a means of measuring temperature. Electrical resistance can be measured very accurately. Siemens' original pyrometer consisted of a platinum wire one millimetre in diameter and one metre long, coiled round a pipe-clay rod and contained in an iron sheath. As the temperature of the wire increased, so did its resistance towards the passage of an electric current through it. Owing to the possibility of contamination of the platinum wire by the heated iron sheath under reducing conditions, the pyrometer was considered unsatisfactory.

The researches of Callendar and Griffiths about 1887 re-established the resistance pyrometer in favour, and the modern type is probably the most accurate and reliable temperature measuring instrument within the range of temperature for which it can be used.

A portable form, as made by the Cambridge Scientific Instrument Co., consists of a thin platinum wire (about 0.01 inch in diameter), wound upon a mica frame or core. The free ends of the coil are connected by stout platinum leads to terminals on the pyrometer head. Two other exactly similar leads traverse the whole length of the pyrometer but do not touch the coil, and they are connected with two other terminals

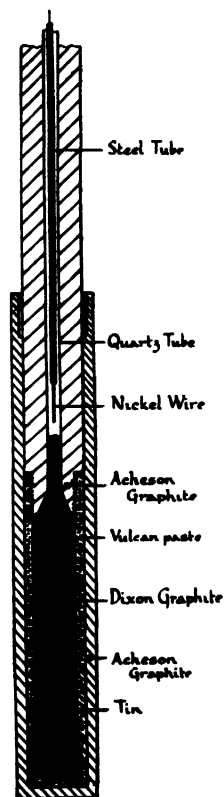


FIG. 46.—THE TIN THERMOMETER.

* *Trans. Faraday Soc.*, 1917-18, 18, 330.

in the pyrometer head. These leads, known as compensating leads, are therefore under exactly the same temperature conditions at all times as the leads from the coil. Any changes therefore in the resistance of the leads due to changes of temperature may be balanced by the resistance of the compensating leads. The whole of the leads and coil are enclosed in a porcelain tube. This tube is inserted into the hot region the temperature of which is to be determined, when the resistance of the coil increases until the region and the tube are at the same temperature. This resistance is then balanced by an opposing resistance in the recorder that is put into circuit by turning a milled head connected

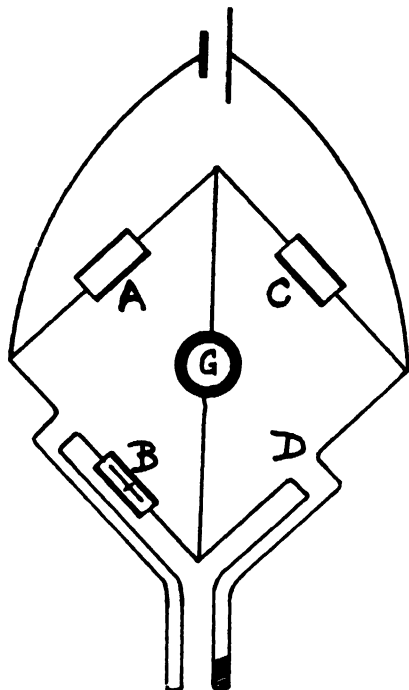


FIG. 47.—THE WHEATSTONE BRIDGE METHOD OF MEASURING ELECTRICAL RESISTANCE.

with it. The balance is indicated by a magnet needle, which points to zero on the scale when the balance is made. The temperature is then read from a second scale. The diagram in Fig. 47 illustrates the Wheatstone bridge method of measuring the resistance which is usually employed. **A** and **C** are fixed resistances of known value, **B** is an adjustable resistance and **D** is the resistance to be measured. When the temperature of the coil and compensating leads is constant, resistance **B** is adjusted to give a zero reading on the galvanometer.

Then

$$\frac{A}{B} = \frac{C}{D} \text{ or } B = \frac{A \times D}{C}.$$

and if **A** is the same as **C**, then **B**=**D**. The reading of the resistance **B** is therefore a measure of the temperature.

¶ Resistance pyrometers are very accurate for temperatures below 900° C., but cannot be used continuously and satisfactorily above this point. The maximum temperature at which it may be used is about 1200° C., but exposure to intense heat for any except very short periods results in destruction of the pyrometer. Pure metal is used for the spiral, since alloys do not show the same changes of resistance to electrical current on heating.

Indicators or recorders may be used with this type of pyrometer, but the difficulty of producing pyrometers with equal resistance renders this form of instrument unsuitable for installations where one recorder serves for several pyrometers. Resistance pyrometers are not so rapid in action as thermo-electric pyrometers. Since the leads are duplicated and used in opposition, readings are independent of the temperature of the pyrometer head and also of the distance that the pyrometer is from the furnace at the taking of the reading. The resistance type of pyrometer is more costly than the thermo-electric, both as regards the instrument itself and the indicator or recorder; it is more difficult to repair, is more liable to get out of order, and requires more skilled attention.

(160) **The Thermo-Electric Type.**—*Historical.*—Seebeck, in 1822, made the discovery that when a junction of two dissimilar metals is heated, an electromotive force is set up at the junction. When the two wires form a closed circuit there are obviously two junctions. Provided the two junctions are at different temperatures, a current will flow round the circuit. This current will be proportional to the difference in temperature between the two junctions if the resistance of the circuit remains constant. By maintaining one of the two junctions, usually termed the "cold junction," at a constant temperature, it is possible to determine the temperature of the second, or "hot junction," by merely measuring the current passing through the circuit.

Pouillet,* some ten years or so later, first applied the principle for the measurement of high temperatures, using an iron-platinum couple and a low-resistance, tangent galvanometer.

Becquerel, about the same time, tried a platinum-palladium couple, but with little success owing to the lack of a reliable galvanometer. His son appears to have been the first to advocate the use and importance of a galvanometer of high resistance. Barus and Tait† replaced the unreliable platinum-palladium couple by one of platinum and platinum-iridium alloy (10 per cent. iridium), which proved much more satisfactory. Shortly afterwards, in 1886, Le Chatelier showed that platinum-rhodium (10 per cent. rhodium) was a more stable alloy than platinum-iridium at temperatures above 1000° C. and adopted the platinum-platinum-rhodium couple as his standard. His work has been confirmed by a large number of workers, and particularly by Day and his colleagues of the Geophysical Laboratory at Washington.‡

* *Compt. rend.*, tome iii., p. 786; *Treatise on Physics*, fourth edition, 1836 vol ii., p. 684.

† See *Bull. U.S. Geol. Survey*, Nos. 54 and 103 (1889).

‡ W. P. WHITE, *Phys. Rev.*, 1906, 28, 499.

(161) **Base-Metal Couples.**—The high price of platinum in recent years has stimulated search for cheaper wires. Most satisfactory of the so-called base metal couples is silver-constantan (copper 60 per cent. and nickel 40 per cent.), which can be used to a temperature of 700° C. Copper may be used to replace silver, but is not nearly so trustworthy as the silver for temperatures above 500° C. For temperatures about 700° C. to 1000° C. either the Hoskins alloys, namely, nickel-nickel-chrome (10 per cent. chromium) and "chromel-alumel" (90 per cent. nickel, 10 per cent. chromium, and 98 per cent. nickel, 2 per cent. aluminium) or a couple of iron-constantan will prove most serviceable.

After a trial of several base-metal thermocouples, one of No. 18 nichrome and No. 12 constantan was found by Woodward and Harrison* to be the most satisfactory couple in an oxidising atmosphere at high temperatures (about 1000° C.). The wires had a single asbestos wrapping, and were further protected by covering with a thick mixture of kaolin and sodium silicate, winding with asbestos cord, and again smearing with a thinner mixture of kaolin and sodium silicate. The couple had a comparatively high electromotive force (E.M.F.)—namely, 63.8 millivolts at 1000° C.—and it maintained its constancy within 10° until the constantan was almost completely oxidised.

(162) **The Choice of Metals and Precautions in Use.**—As already mentioned, the platinum-platinum-rhodium couple is the standard for laboratory measurements between 300° C. and 1400° C., and when properly protected it has been successfully employed commercially. It is usually free from injurious inhomogeneities and withstands long exposure to high temperatures without serious deterioration. For precise temperature reading it is necessary that each wire and portion of the wire of a thermocouple shall be of exactly similar composition and possess the same physical properties in order to avoid change of reading with change of depth of insertion of the thermocouple into the furnace. The disadvantages in connection with this couple are its cost and its comparatively low sensitivity.

For temperatures up to 300° C. a copper-constantan couple is very useful, being inexpensive, and much more sensitive than the platinum-platinum-rhodium couple, whilst both wires can be obtained fairly homogeneous and of convenient diameter. When temperatures up to 1000° C. are to be measured, iron-constantan or chromel-alumel couples are most generally useful. Copper and constantan readily oxidise at temperatures above 300° C., the E.M.F. of the couple falls, and the wires become brittle and finally break. Iron oxidises fairly readily and should be used (with constantan) in a reducing atmosphere, whilst the Hoskins alloys, chromel-alumel, should be used in an oxidising atmosphere.

At temperatures above 1000° C. all these couples rapidly deteriorate.

In Table LXIX., on p. 211, are shown the relative sensitivities of various couples.

Not all metallic couples are suitable. Iron-copper gives an E.M.F. which increases with temperature up to a certain point, then falls off and finally reverses direction.

Before calibration, all high temperature thermocouples should be

* *Chem. and Met. Eng.*, 1917, 16, 647.

annealed by heating to a temperature considerably higher than any to which they may be exposed in use. Parasitic E.M.F.'s which might be developed between hard and soft portions of the wires are thereby eliminated.

TABLE LXIX.—E.M.F.'s OF VARIOUS THERMOCOUPLES.*

Couple.					Approximate E.M.F. in Millivolts at 500° C.
Pt.-Pt. Rh. (10 per cent. Rh.)	4.4
Pt.-Pt. Ir. (10 per cent. Ir.)	7.4
Ni.-Ni. Cr. (10 per cent. Cr.)	21.0
Ni.-Fe	12.0
Fe.-Constantan	26.7
Ag.-Constantan	27.6
Cu.-Constantan	27.8

It is obvious that the melting-points of the wires must be considerably higher than any temperature they will be used to measure, and accordingly the limit of thermo-electric pyrometry is reached at 1400° C. Platinum-platinum-rhodium pyrometers may be used for short periods at 1500° C., but cannot be used for long periods at this temperature and remain accurate in indication.

Corrosion of wires may be prevented by sheathing them in silica or porcelain tubes, but a really satisfactory sheath has yet to be discovered, and in this respect zirconia, alundum, or carborundum may prove useful.

The wires of the couple may be joined together by twisting, welding, or soldering, depending upon the actual compositions of the wires. Fusion or welding is to be preferred, since twisted or soldered connections are liable to cause interruptions in the circuit, particularly when the wires become oxidised. Copper-constantan and iron-constantan junctions may be formed by silver solder, using borax as flux, but even in this case welding is preferable.

The junction of the wires which is introduced into the furnace is known as the "hot-junction." The wires may be continued to the indicator, and where the wires join the terminals we have the "cold-junction." In practice this arrangement is not possible, since if the wires are platinum and platinum-rhodium the cost will be too great, and further, the hot junction being at a relatively high temperature, the thermocouple itself, at any rate over part of its length, will be raised in temperature and the indicator—the cold junction—may be at a different temperature from that at which the original calibration was made. These changes in the temperatures of the thermocouple and indicator will change their electrical resistance, and consequently the indicator will no longer show directly the temperature of the hot junction. For these reasons it is usually necessary to insert into the thermocouple circuit an additional "ballast" resistance. This ballast resistance is made of material which in itself does not change in resistance with

* WHIPPLE, *Proc. Inst. Mech. Eng.*, July 29, 1913.

change in temperature, and it is made so large, in comparison with the other resistances of the circuit, that any change in those other resistances due to change in their temperature is relatively small and without appreciable effect upon the indicator reading. This modification is shown at **B** in Fig. 48.

Unless the distance between the hot junction whose temperature is to be measured and the indicator which makes the measurement is very short, the arrangement at **B** is not convenient, and if renewal of the thermocouple should be necessary, the whole length from the hot junction

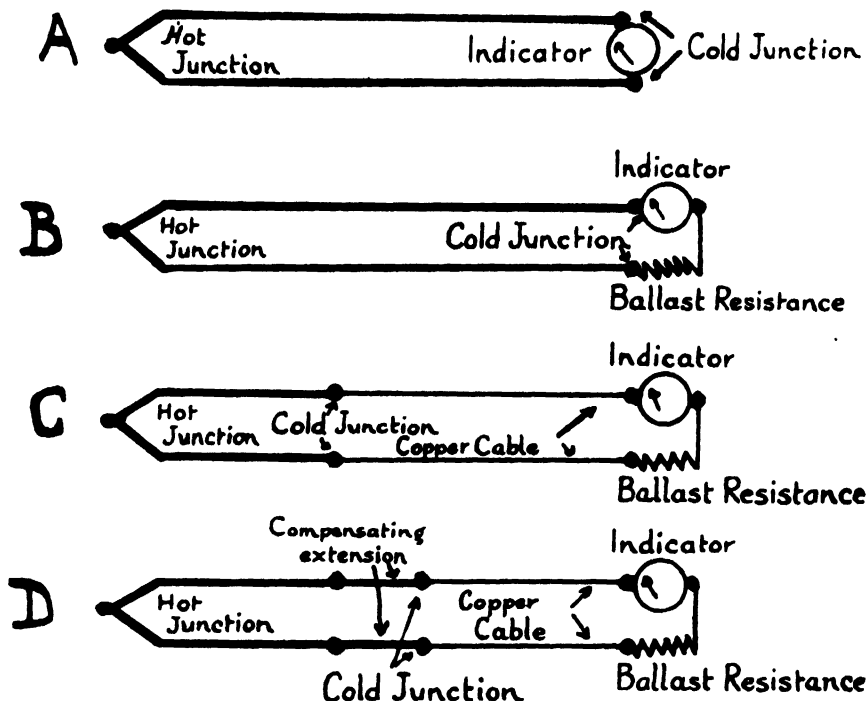


FIG. 48.—DEVELOPMENTS OF THE THERMOELECTRIC CIRCUIT.
(By courtesy of the Foster Instrument Company, Letchworth, Herts.)

to the cold junction would have to be renewed. It is therefore convenient, usually, to use a thermocouple of relatively short length and to connect its cold junction to the indicator by twin copper cable, in which case the ballast resistance is usually included inside the indicator case. The electrical resistance of the copper cable will change if its temperature changes, and this makes it necessary for the ballast resistance to be still larger, in order that it may obliterate the effect of change in resistance of the rest of the circuit.

It was stated above, as a condition for the indicator to be calibrated directly in temperature, that the hot junction and the cold junction must be at known temperatures; if the hot junction remains at a steady

high temperature, but the relatively low temperature of the cold junction should change, the reading of the indicator will change, because the current it is measuring depends upon the *difference* in temperature between the hot junction and the cold junction. It is therefore necessary, if the indicator is to be direct reading in temperature, that the cold junction shall be maintained at the temperature which existed when the instrument was calibrated, otherwise a correction will be necessary to the reading.

(163) **The Calibration of the Thermocouple.**—The cold junction is maintained at a steady temperature, for instance 0°C . (32°F .) and, before connecting the thermocouple to the indicator, the indicator pointer is at the zero or lowest position on the scale and that position is marked 0°C . The hot junction is then heated to a steady known temperature—say, 100°C .—the scale then being marked “100” at the position taken up by the pointer; similarly, the hot junction may be heated to 200°C . and the scale marked correspondingly, and this process may be carried on up to the maximum reading of the scale, maintaining the cold junction all the time at 0°C . (It is sometimes convenient to leave out the “o’s,” specifying the scale as “Hundreds Centigrade” and figure the calibration points 1, 2, 3 and so on.) By this method of calibration, each successive step in the scale has been divided according to the current proportional to that difference of temperature; for instance, the width of scale between “100” and “200” is proportional to the current which would flow if the cold junction were at 100°C . and the hot junction at 200°C ., and so on all up the scale. Following the explanation above, it will be evident that if the hot junction were maintained at, say, 300°C . and the cold junction, which had been previously at 0°C ., were allowed to heat up to 10°C ., there would be less current flowing because there would be less difference in temperature between the hot junction and the cold junction, although the hot junction has remained at a steady temperature. This difference in current would be represented, on the scale, by the distance from “0” to “10,” so that, if we disconnect the thermocouple from the indicator and set the pointer at 10°C ., on reconnecting, the indicator will read correctly the temperature of the hot junction because we have added, on the scale, the amount which we lost by the rise in temperature of the cold junction from 0° to 10° .

Similar results will follow for any particular temperatures of the cold and hot junctions; provided the pointer is set to the actual cold junction temperature before the indicator is connected to the thermocouple, the pointer will then always point to the true temperature of the hot junction. This method of setting the pointer is at once simpler and less liable to error than the older method of setting the pointer at 0°C . (32°F .) and making an arithmetical correction to the observed reading.

The thermocouple now being supposed relatively short, as in condition **C**, Fig. 48, it is possible that if the hot junction is inserted into a furnace the cold junction will be liable to change its temperature due to radiation from the furnace and thus involve re-setting the pointer of the indicator at inconveniently short periods. To get over this difficulty, the arrangement as shown at **E** may be adopted. The thermocouple is joined at its outer end to a **compensating extension**—that is, to two metals or

alloys which are thermo-electrically interchangeable with the thermocouple—so that, in effect, the cold junction is removed to such a distance from the furnace that its temperature will remain conveniently steady. In this form, as at **D**, a practical industrial thermocouple pyrometer is made.

The further temperatures at which the thermocouple may be calibrated are those indicated as "fixed points" in Table LXVIII.

(164) **The Indication of Temperature.**—There are two methods which may be used to measure the E.M.F. produced by the difference in temperature between the hot and cold junctions.

The *potentiometric method* is undoubtedly the more accurate, as it is a "null" or balancing one, thus eliminating any errors due to the re-

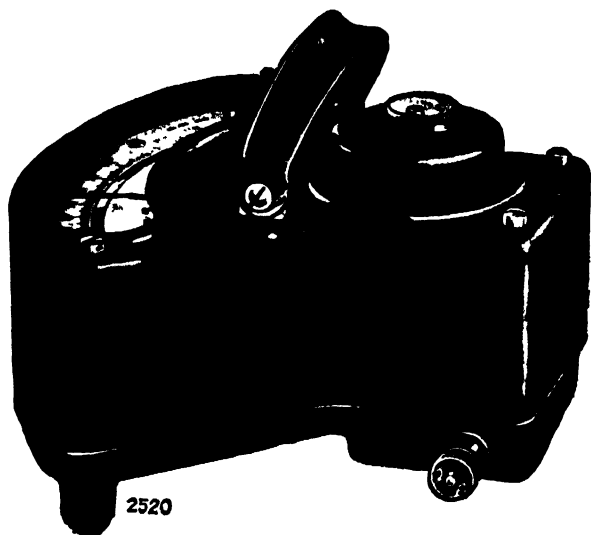


FIG. 49.—THE "CAMBRIDGE" PORTABLE INDICATOR.

(By courtesy of the Cambridge and Paul Instrument Company, Ltd., London.)

sistance of the leads and couple. The E.M.F. from the thermocouple is balanced against that given by an accumulator, the E.M.F. of which has been found by means of a standard cell.

However, the "direct" method of measurement of millivolts is almost invariably used in industrial practice. The number of millivolts generated in the thermo-couple circuit is measured on a direct deflection galvanometer or "millivoltmeter." This instrument is usually of the moving coil type, which is not affected by moving masses of iron or stray magnetic fields. It is advisable that it should have a high resistance.

The range of temperature over which it can be made to operate depends upon the thermocouple employed, the resistance of the galvanometer coil, and the resistance placed in series with the coil.

The E.M.F. developed is independent of the thickness of the wire, and hence base-metal couples of the Hoskins alloys type may be made of thick wire, and since they develop a comparatively high E.M.F., less sensitive galvanometers are required and the overall cost is less.

In Fig. 49 is shown the standard pattern portable indicator made by the Cambridge Scientific Instrument Co. The indicator is enclosed

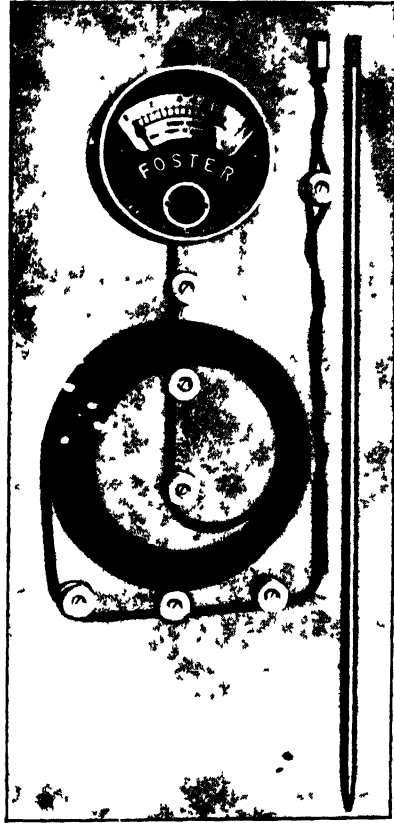


FIG 50.—THE "FOSTER UNIT" INDICATING OUTFIT
(By courtesy of the Foster Instrument Company, Letchworth, Herts)

in a dust-proof metal case fitted with a handle for carrying. It does not require accurate levelling, but may be set down on a workshop bench and read at once. The indicator is fitted with a fine pointer, and a mirror is placed below the scale to avoid parallax errors. An adjustment is provided to enable the pointer to be set to the cold junction temperature before taking a reading.

A wall type indicating outfit of the "unit" class manufactured by the Foster Instrument Co., of Letchworth, is shown in Fig 50.

Since joints may be made in the lead wires of a pyrometer without affecting the E.M.F. (provided the joints are at the same temperature), keys and switches may be introduced into the circuit. The thermoelectric pyrometer is therefore quite suitable for installations. One indicator may be connected to a number of pyrometers through switches and any one of them read at any time. A wall type indicator with a twelve-way switch (eleven pyrometers and "off") is shown in Fig. 51. This instrument is made by the Wilson-Maeulen Co., of New York, and is installed at the Pennsylvania Wire Glass Co., Dunbar, Pa. It will be noted that the indicator is protected by a special fume-proof glass cover.



FIG. 51.—THE "WILSON-MAEULEN" INDICATOR.
(By courtesy of the Wilson-Maeulen Company, New York)

(165) **The Recording of Temperature.**—For the autographic recording of very small and rapid changes of temperature, the photographic arrangement originally due to Le Chatelier, and then to Roberts-Austen, is still the only method available. In the Roberts-Austen form the path of a spot of light, reflected from a small mirror on the needle of the galvanometer, is recorded on a moving photographic plate. This form of recorder is of no use except for accurate research, since one cannot see the record until after the photographic plate has been developed.

For common use "thread-recorders" are very suitable and find extensive employment.

In the majority of these recorders the galvanometer pointer or "boom" is depressed intermittently by clockwork or some simple

electrical mechanism on to either an inked thread or typewriter ribbon which is pressed on to a chart mounted on a rotating drum (clockwork-driven), the resulting record being a series of inkmarks.

A thread recorder made by the Cambridge Scientific Instrument Co. is shown in Fig. 52. The recorder consists of a galvanometer with either suspended or pivoted coil, the pointer of which is automatically depressed by clockwork every minute or half-minute on to a chart covering a drum. A thread impregnated with ink passes between the pointer and the chart, and when the pointer is depressed it forces the thread on to the paper and so gives a permanent record of the temperature at the moment in the form of a dot. As the drum is made to rotate slowly the successive dots merge into a line. With this method of recording pen friction is entirely avoided. The drum is arranged to make one revolution in

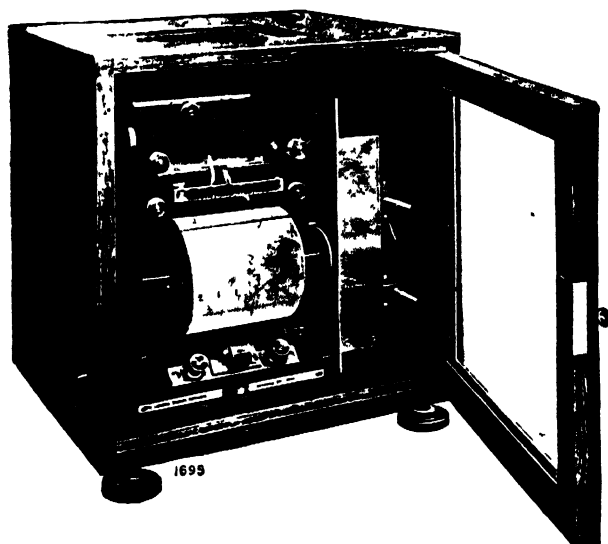


FIG. 52.—THE "CAMBRIDGE" THREAD RECORDER.

(By courtesy of the Cambridge and Paul Instrument Company, Ltd., London.)

25 hours, or, by means of a simple change-speed arrangement, in two hours five minutes. The record for the previous few hours is always visible, and an engraved scale is fixed over the pointer so that the actual temperature at any moment can be observed. The impregnated thread only requires renewing at long intervals.

A record made on a recorder of this type is reproduced in Fig. 146.

A recorder of a different type is made by the Foster Instrument Co. (see Fig. 53).

Instead of moving a pointer over a scale this instrument moves a pen and pen arm over the chart. In order to avoid the errors which would result from friction if the pen were constantly pressing upon the surface of the chart, and also to avoid smudging of the record, which might arise under the same circumstances, the pen is normally out of

contact with the chart, but is pressed thereon once each minute, leaving an indelible ink dot. Having made a dot upon the chart the pen is deflected to the side of the case and is then pressed upon an ink drum, thus receiving a fresh supply of ink for the next dot. In this manner a chain of dots is made upon the chart, these dots joining up into a continuous line with normal working.

The chart is rotated by a clock mechanism, the same mechanism being employed to deflect the pen to the ink drum and to press it upon the drum and subsequently upon the chart. The design is such that it is suitable for work under severe industrial conditions where more delicate and complicated instruments would be likely to break down. The case is fitted with a dust seal, the moving system and clock are separately protected inside the main case, the whole being damp-proof and insect-proof, and, therefore well suited to tropical and other export conditions.

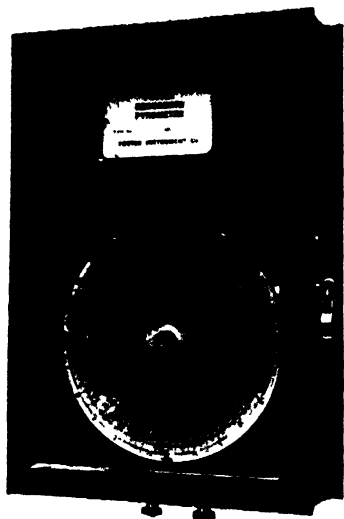


FIG. 53.—THE "FOSTER" AUTOMATIC RECORDER.

(By courtesy of the Foster Instrument Company, Letchworth, Herts.)

The chart being circular, the whole of the record can be seen at a glance without disturbing the recorder in any way; this is not possible with a drum type instrument. The chart is arranged to rotate once in twenty-four hours, but where desired specially the recorder may be allowed to run over several days, as, for instance, in recording a temperature which rises slowly to a maximum, remains steady for a period and then falls slowly. The attachment and removal of the chart is an operation of only a few seconds; it has been so simplified that the ordinary furnace man can change the chart with ease. When the door of the recorder is opened, the pen and pen arm are automatically lifted off the chart and carried to the left, to protect them from damage when inserting a new chart, and they are held out of the way until the door is closed

again, having a central hole, the chart may be filed very easily for reference afterwards. On each chart there is provision for writing the date, furnace number and job in hand

A temperature record produced on one of the charts is reproduced in Fig 145

With thread recorders an arrangement may be made for two or more simultaneous records on one chart The "Tapalog," made by the

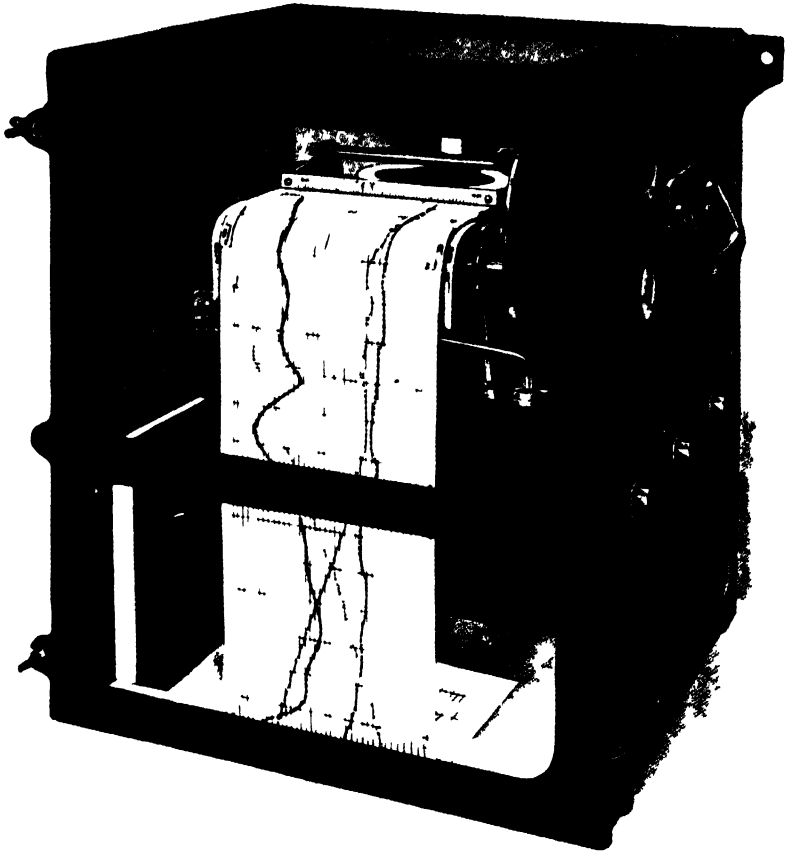


FIG. 54 —THE "WILSON-MAEULEN TAPALOG."
(By courtesy of the Wilson-Maeulen Company, New York)

Wilson-Maeulen Co., is a pyrometer recorder for single or multiple records, which are obtained in from one to six colours, representing temperatures at one to six points, each readily distinguishable from the others no matter how much they cross one another. The instrument (see Fig. 54) is driven by three dry cells. The automatic switch located

inside the tapalog is a commutator of platinum brushes on gold slide wires with bakelite insulation, and the switch is synchronised with the ribbon shift or colour changing device.

The six-record tapalog, shown on the left of Fig. 55, is connected to the annealing lehrs, and the three-record instrument on the right to the tank furnaces. Out in the furnace room there is another indicator and switch for the use of the furnacemen (see Fig. 56).

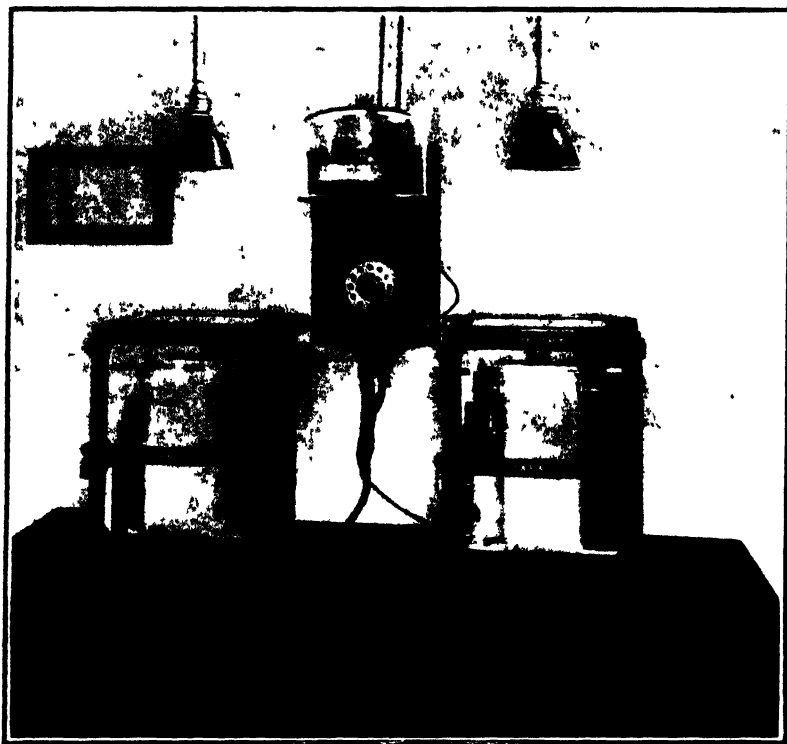


FIG. 55.—"TAPALOGS" CONNECTED TO LEHRS AND FURNACES.

(By courtesy of the Wilson-Maeulen Company, New York)

(166) The Advantages of the Thermo-electric Type of Pyrometer.—

(1) Simplicity. No special experiment is required when a temperature is to be determined.

(2) Cheapness.

(3) Adaptability.

(4) Ease of repair.

(5) Robustness.

(6) Suitability for centralised control.

The only disadvantage is the liability to error due to the change of temperature of the cold junction, but, as already indicated, it may be avoided

(167) **The Radiation Type.**—As has been mentioned previously, all bodies radiate heat to their surroundings, and the hotter the body the greater the amount of heat it will radiate. Above a temperature of about 500°C . the energy radiated is partially visible as light, and the remainder invisible as heat.

In radiation pyrometers the energy of the total radiation is measured in various ways by the heat effect which it produces. The most common method employed is to focus the radiation upon a thermocouple, the E.M.F. so produced being employed to measure the temperature in the manner already described.



FIG. 56.—PYROMETER SWITCHES AND INDICATOR IN FURNACE ROOM.
(By courtesy of the Wilson-Maeulen Company, New York.)

Now the radiation emitted by any substance depends on the nature of the substance and the condition of its surface as well as upon the temperature. Kirchoff first propounded the idea of a *black body* as being one which would absorb all radiations falling upon it and from which no radiations would be reflected or transmitted. He also showed that the radiation from such a black body would be a function of the temperature alone and identical with the radiation inside an enclosure, all parts of which have the same temperature. The ordinary commercial furnace practically fulfils black body conditions.

Stefan first stated that the energy radiated by a black body was proportional to the fourth power of the absolute temperature, and

Boltzmann later deduced the same law by a thermodynamical method. As a result of their work was enunciated the "fourth power" or "Stefan-Boltzmann" law, which may be expressed mathematically in the following manner:

$$E = k (T^4 - T_0^4)$$

where E is the total energy radiated by the body when at a temperature T to its surroundings at a temperature T_0 . Both temperatures are "absolute"—i.e., are measured from the absolute zero.

The ordinary commercial furnace practically fulfils black-body conditions. Accordingly, if a fireclay tube is inserted with its closed end in the furnace and uniformly heated, the temperature may be measured with a radiation pyrometer focussed on the heated part of the tube through the open end outside the furnace.

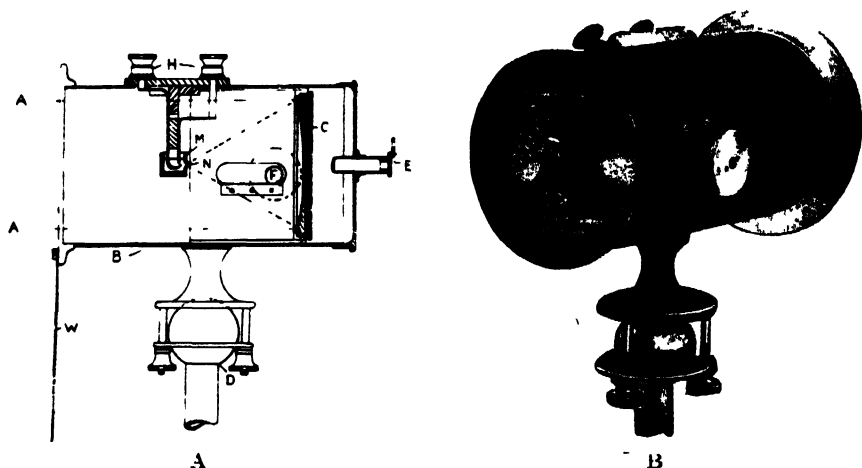


FIG. 57.—THE "FÉRY" RADIATION PYROMETER.

(a) Diagrammatic sketch of construction; (b) general view.

(By courtesy of the Cambridge and Paul Instrument Company, Ltd, London.)

Radiation pyrometers are usually graduated to read black-body temperatures, and when the conditions do not conform to those of the black body, then the reading will be low.

At temperatures above 1300°C ., where the types of pyrometers previously described are subject to a number of practical difficulties, radiation pyrometers may be advantageously employed.

(168) **The Fery Radiation Pyrometer.**—The first practical total radiation pyrometer was invented by C. Fery,* and it remains one of our best high temperature pyrometers. As made by the Cambridge Scientific Instrument Co., the pyrometer consists of a telescope which is focussed on the hot body, the heat rays being received on a concave mirror and brought to a focus on a small thermocouple. The E.M.F.

* *Compt. rend.*, 1902, 134, 977.

produced by the consequent heating at one junction of the thermocouple is measured on an indicating or recording galvanometer calibrated to give direct temperature readings.

The optical arrangement of the telescope is illustrated in section by Fig. 57. The heat rays **A** from the furnace are received on the concave mirror **C** and brought to a focus at **N**. Looking through the eyepiece **E** the observer sees an image of the furnace in the small mirror **M**, and is able to point the telescope towards the exact spot of which the temperature is required and to focus it on that spot. The small sensitive thermocouple is situated just behind a small hole in the mirror **M**, and becomes heated by the rays passing through this hole.

An ingenious device is fitted on the telescope to make the operation of sighting and focussing the instrument as simple as possible. The mirror **M** in which the observer sees the image of the furnace actually consists of two small, semicircular, wedge-shaped mirrors fixed together. If the instrument is correctly focussed, the appearance is as shown in the centre diagram of Fig. 58, in which the outer circle represents the mirror, the shaded portion the reflected image, of the hot body on which the telescope is sighted, and the black centre is the sensitive element of

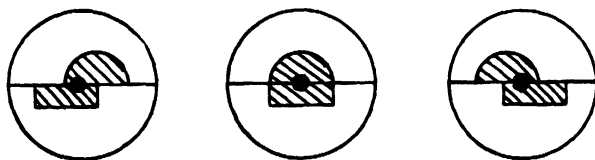


FIG. 58.—THE FOCUSING OF THE "FÉRY" PYROMETER.

(By courtesy of the Cambridge and Paul Instrument Company, Ltd., London.)

the pyrometer, which must be covered by the image of the hot body. If the focus is too short, the image appears split in two parts, as in the left-hand diagram, whilst if it is too long the appearance is similar but reversed, as in the right-hand diagram. Turning the knurled head attached to the pinion **F** (see Fig. 57) causes the upper and lower half images to slide on one another, so that it is easy to get the exact focus, and no personal error can creep in. The size of the aperture or body sighted on, and the distance of the telescope from it, do not, within wide limits, affect the temperature readings. It is only necessary for the body sighted on to be of a size that its image will overlap on all sides the sensitive element in the telescope (see Fig. 58).

To secure this with the Féry Radiation Pyrometer the size of the object sighted on must be at least 1 inch (25 mm.) in diameter for every 2 feet (60 cm.) of distance between the telescope and the object.

The pyrometer may be sighted upon an opening in the furnace wall. When the opening is small compared with the distance behind it of the opposite furnace wall, the radiation issuing through it is independent of the quality of the radiating surfaces and is the same as if those surfaces were perfectly "black." Flames interposed between the observation hole and the furnace wall behind, provided they are at the same temperature as the furnace, do not affect the reading. Even when their

temperature differs from that of the furnace, such flames are too transparent to absorb or emit any perceptible radiation, so that in practice

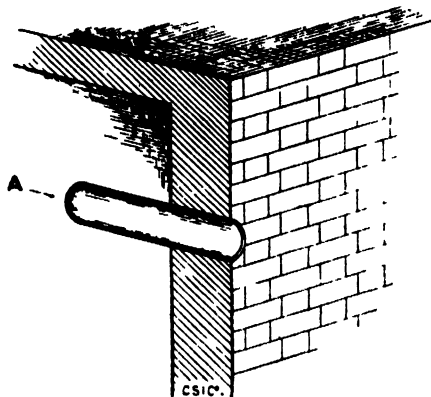


FIG. 59.—A PYROMETER-SIGHTING TUBE IN A FURNACE WALL.
(By courtesy of the Cambridge and Paul Instrument Company, Ltd., London.)

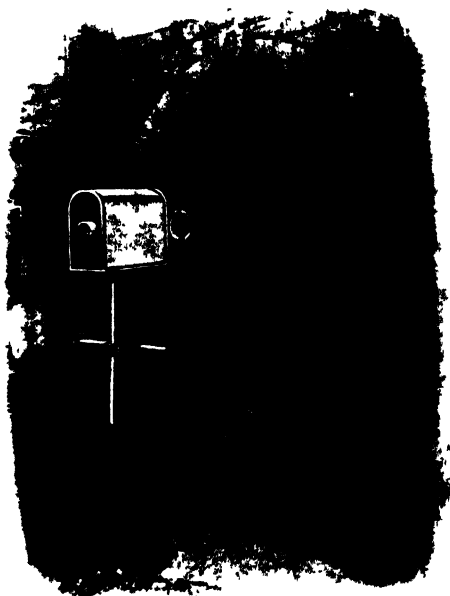


FIG. 60.—"FÉRY" TELESCOPE, WITH COVER, MOUNTED OUTSIDE A POTTERY KILN.
(By courtesy of the Cambridge and Paul Instrument Company, Ltd., London.)

no error arises from this cause. Where it is not practicable to have the pyrometer sighted on an existing opening in the furnace, or where

no such opening is desired, a fireclay or silica tube, inserted into the furnace wall, gives opportunity for the situation of a permanent outfit (see Figs. 59 and 60).

(169) **The Foster "Fixed Focus" Radiation Pyrometer.**—C. E. Foster* has introduced a modification of the Fery pyrometer by putting the small thermocouple (**D**, Fig. 61) and the aperture (**EF**) facing the source of energy at the conjugate foci of the mirror **C**.

Fig. 61 shows a diagrammatic section of the receiving tube, approximately to scale. At the front end of the tube **MNPQ** is an aperture **EF**.

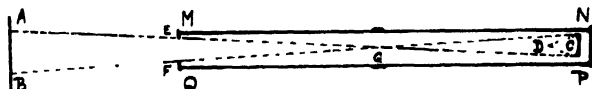


FIG. 61.—DIAGRAMMATIC SECTION OF "FOSTER" RECEIVING TUBE.

(By courtesy of the Foster Instrument Company, Letchworth, Herts.)

Radiant heat from the hot body such as **AB** enters the aperture **EF** and is received by the concave mirror **C**. The proportions of the instrument are arranged so that a body **D**, sensitive to heat, is where the mirror **C** forms a focused image of the aperture **EF**.

If the aperture **EF** could be placed in contact with the hot body, a focused image of the hot body surface, limited by the aperture **EF**, would be formed by the mirror **C** on the thermocouple **D**. This image would be not only a light image, but also a "heat image," and would therefore cause a rise in the temperature of **D** depending on the radiant energy given out by the hot body. It is by means of this rise in temperature that the actual measurement is made.



FIG. 62.—A "FOSTER" RECEIVING TUBE WITH MIRROR CELL REMOVED

(By courtesy of the Foster Instrument Company, Letchworth, Herts.)

The action of the instrument is independent of the distance from the hot body, provided a certain maximum working distance is not exceeded. This maximum distance is given by the simple rule: the maximum working distance is a fixed multiple of the diameter (or smallest transverse dimension) of the hot body. This fixed multiple is called the "distance factor," which is generally taken as ten.

It is not usually necessary to measure accurately the diameter of the hot body or the working distance therefrom, because any distance less than the above limit will make no difference to the reading. To meet

* *Trans. Amer. Electrochem. Soc.*, 1910, 17, 223.

those cases where the margin for pointing is small, for instance, owing to the hot body being small or the working distance necessarily large, a sighting device is incorporated in the tube whereby the user can verify accurately if the tube is within the requisite working distance and correctly pointed.

Fig. 62 shows a receiving tube as manufactured by the Foster Instrument Co., with the mirror cell removed, whilst in Fig. 63 is illustrated a tube with fixed housing in a furnace wall.

Indicators or recorders, with appropriate scales, may be used with the Féry and Foster radiation pyrometers as with thermo-electric pyrometers.

(170) **The Optical Type.**—In optical pyrometers use is made of the visible radiation from a hot body. Becquerel in 1864 suggested that the measurement of the intensity of red radiations emitted by incandescent bodies might be employed as an indication of the temperatures

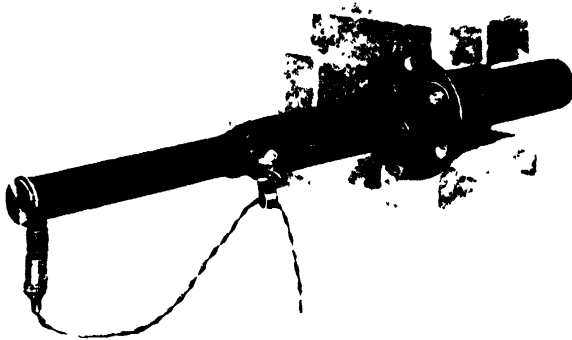


FIG. 63.—" FOSTER " FIXED HOUSING IN A FURNACE WALL.
(By courtesy of the Foster Instrument Company, Letchworth, Herts.)

of the bodies. Some considerable time later, Le Chatelier* invented the first practical optical pyrometer. The instrument was really a form of photometer, since the luminous radiation from the body under examination was matched against that from a standard lamp. The Féry absorption pyrometer is a modification of Le Chatelier's pyrometer, and has been found very useful for measuring the temperature of incandescent filaments and other extremely hot but small bodies.

(171) **The Wanner Pyrometer.**—This pyrometer (see Fig. 64) is another of the photometric type. Light from a six-volt incandescent lamp used as comparison, and from the object whose temperature is sought, enters the slits U_1 and U_2 respectively, the two beams being rendered parallel by the compound lens J and dispersed into a continuous spectrum by the prism system B . The biprism lens C produces deviations in the beams of such an amount that images from the two sources are brought side by side. The arrangement of the remaining parts is such

* See *L'Industrie électrique*, April 10, 1892; also *Journal de Physique*, May 1, 1892.

as to bring before the Nicol prism analyser **B** a field, half of which is illuminated by red light from the spectrum of U_1 and the other half by red light from the spectrum of U_2 , the two halves being polarised at right angles to one another. If the analyser is at an angle of 45° to the plane of polarisation and U_1 and U_2 are equally illuminated, the field is uniformly bright. If they are unequally illuminated one half the field will appear brighter than the other, and they are equalised by turning **B**, which carries a scale that can be interpreted in terms of degrees of temperature.

(172) **The Cambridge Optical Pyrometer.**—This pyrometer is a practical, convenient, and, at the same time, accurate instrument which can be successfully used by unskilled workmen. Temperatures from 700°C . upwards are read directly upon clear, open scales.

The instrument may be regarded as a photometer, in which, by simply rotating the eye-piece, a beam of selected monochromatic light from the hot body is adjusted to equal intensity with a beam of similar

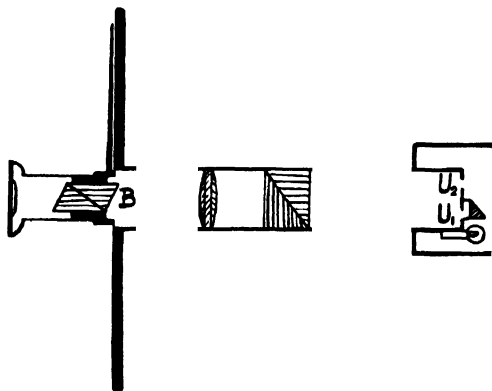


FIG. 64.—THE "WANNER" PYROMETER.

light from an incandescent electric lamp. It is not a colour-matching instrument, and perfectly accurate readings can be taken by an observer who is colour-blind.

The general arrangement of the instrument is shown in Fig. 65 and includes:

A. The pyrometer, consisting of the optical system, the electric lamp, the shield carrying the temperature scale and pointer.

B. The carrying case with fittings for fixing the pyrometer and standard lamp for checking the calibration.

C. The four-volt accumulator, ammeter and regulating resistance.

D. The standard amyl-acetate lamp.

E. The adjustable tripod-stand.

Somewhat similarly to the Wanner pyrometer, it has two holes behind the enlarged part in the front of the pyrometer. Light from the object under observation passes through one and the light from the lamp through the other. These beams of light then pass through a

system of lenses and prisms, are polarised in different planes, and rendered monochromatic by means of red glass* in the eye-piece. Finally, the two beams of light pass through a single eye-piece. The observer sees an illuminated circular field divided into two semicircles. One semicircle is filled by an image of the hot body under observation, and the other is uniformly illuminated by the electric lamp. The two semicircles are brought to an equal intensity of illumination by turning the eye-piece to which the scale pointer is directly attached. In this manner the unknown rays are compared with those of known intensity from the electric lamp.

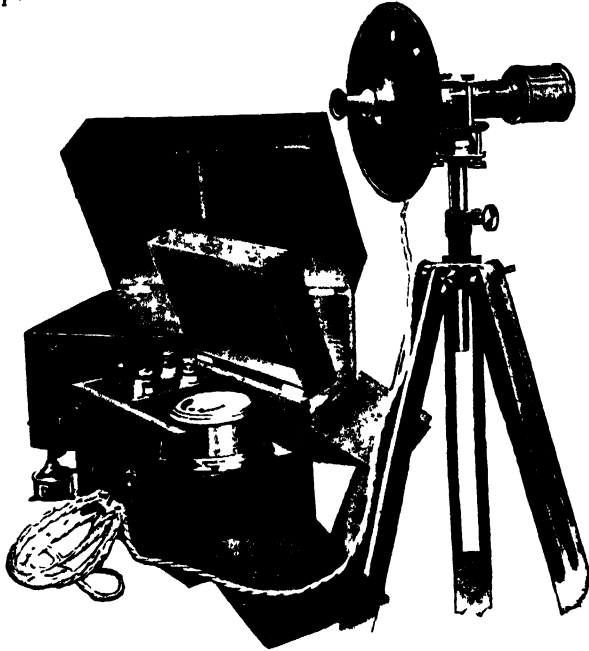


FIG. 65. THE "CAMBRIDGE" OPTICAL PYROMETER.

(By courtesy of the Cambridge and Paul Instrument Company, Ltd., London.)

As the accuracy depends upon the constancy of the light from the electric lamp, a small ammeter and regulating resistance are fitted in the box containing the accumulator to ensure that, whatever the voltage of the battery may be, the current passing through the lamp is constant. To ensure that the candle power of the lamp shall remain constant over long periods as the filament ages, provision is made for calibrating the instrument from time to time against a standard amyl-acetate lamp, and thus ascertaining the reading of the ammeter when the electric lamp is giving the correct illumination. This test need only be made at long intervals and the standard lamp need not be carried into the works.

* In the Wanner pyrometer rays of the same type are obtained spectroscopically and are therefore truly monochromatic.

Optical pyrometers of the types described are, of course, subject to black-body conditions in the same way as total radiation pyrometers. They can only be used for single observations, and are no use for recording purposes, but they may be used under circumstances where other pyrometers cannot be used and, in addition, are cheaper.

(173) **The Wedge Optical Pyrometer.**— This instrument, manufactured by the Optical Pyrometer Syndicate, London, consists of a brass tube furnished with a small telescope, so arranged that the objective of the telescope focuses the image of the heated body on a movable prism

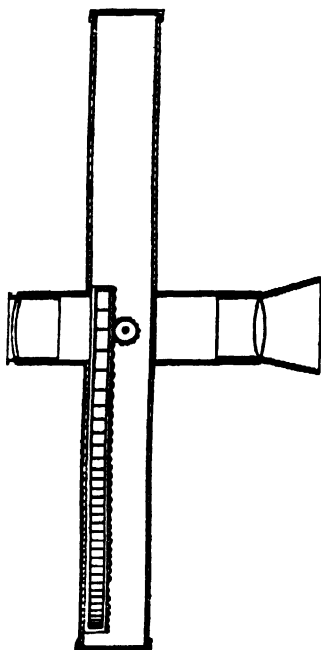


FIG. 66.—A SECTION OF THE " WEDGE " PYROMETER.

(By courtesy of the Optical Pyrometer Syndicate, London.)

placed inside the tube. The eye-piece of the telescope then reveals the magnified image on the prism, while a shield prevents any exterior light from reaching the eye. At one side of the tube is a milled head actuating a rack and pinion arrangement, which moves the prism through the field of vision. The chief feature of the pyrometer is the glass prism, which from top to bottom is graduated in depth of colour; that is to say, while a moderately hot body would be visible through the lightly tinted portion, it would be invisible through the heavily coloured portion. Thus there is a certain point in the prism where the emitted light from the hot body is just eclipsed. When commencing to take a reading the prism is so placed that the lightly tinted part is in the field of vision, and by turning the milled head the depth of colour is progressively

increased (the object meanwhile appearing darker and darker) until the object just disappears. This point gives the actual temperature, and on glancing at the scale, degrees Fahrenheit or Centigrade may be read off direct. A section of the pyrometer is shown in Fig. 66, and its general appearance is seen in Fig. 67.

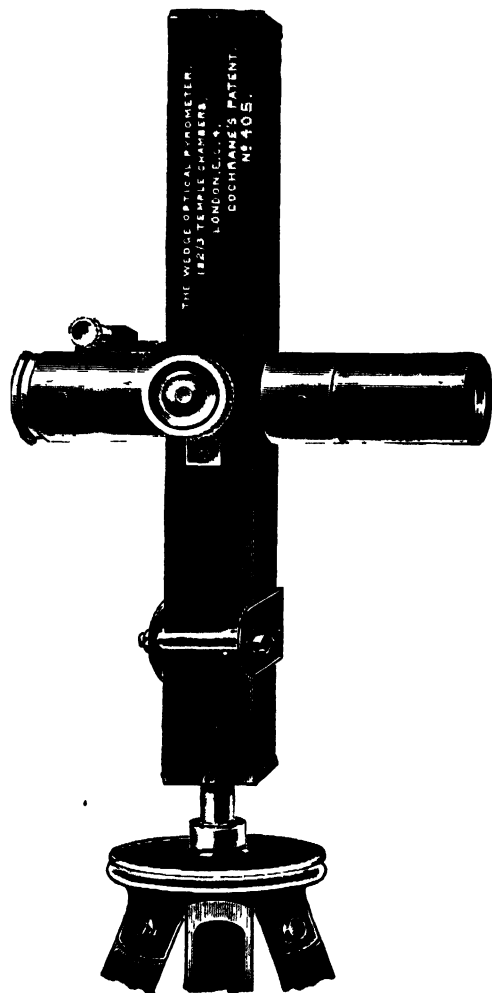


FIG. 67 —THE "WEDGE" PYROMETER ON STAND.
(By courtesy of the Optical Pyrometer Syndicate, London.)

With a little practice a high degree of accuracy may be obtained, and the instrument has been found to compare very favourably with those involving the use of expensive thermo-elements, and electrical recording apparatus. What is more to the point, however, is the fact

that the "Wedge" pyrometer has little to get out of order, and there is no likelihood of its being put out of adjustment by constant use.

Fig. 68 shows an observer in the act of taking a reading with the Wedge pyrometer. This instrument is, of course, very cheap, easy to



FIG. 68 —READING A TEMPERATURE WITH THE "WEDGE" PYROMETER
(By courtesy of the Optical Pyrometer Syndicate, London)

read, and complete in itself. Though not so accurate as certain other types of pyrometer, it nevertheless furnishes a simple means of temperature measurement which may be put into the hands of any workman.

CHAPTER XVIII

FUELS

(174) **The Classifications of Fuels.**—It is customary to include under the name fuels all substances which, on being burned in air under suitable conditions, generate heat which can be used economically for industrial or domestic purposes. They may be solid, liquid, or gaseous in form. Each separate form includes both natural and artificial types, but, with the possible exception of natural gas and mineral oils, fuels are of vegetable origin, and may be regarded as derived from wood-fibre (cellulose) frequently associated with material of a resinous nature. In Table LXX. the various fuels which are used as sources of the heat required in glass furnaces are classified. Those of minor importance will only be discussed very briefly.

TABLE LXX.—A CLASSIFICATION OF FUELS USED IN THE GLASS INDUSTRY.

<i>Form.</i>	<i>Natural.</i>	<i>Artificial.</i>
I. <i>Solid</i> ..	(A) wood; (B) peat; (C) lignite; (D) coal	(E) coke; (F) briquettes.
II. <i>Liquid</i> ..	(A) natural oils such as petroleum oils	(B) distilled oils such as tar oils.
III. <i>Gaseous</i> ..	(A) natural gas	(B) coal gas; (C) coke-oven gas; (D) producer gases.

(175) **Solid Fuels.**—(A) **WOOD.**—Wood is only used as fuel in glass furnaces where other and better fuels cannot be obtained easily or at a reasonable price. It is still employed on the Continent of Europe; in fact, during the year 1920, of one hundred and fifty-six factories in Czecho-Slovakia, fifteen were using wood as the sole fuel and a further twenty-one were using wood and coal. The combustible ingredients of wood are carbon and hydrogen, of which there are usually about 40 per cent. of carbon and 5 per cent. of hydrogen in the air-dried sample. Oxygen is present in combination to the extent of about 30 per cent. and, when "air dried," wood also contains about 20 per cent. of moisture. Wood is not a good fuel, but where it is used, the ashes, consisting of oxides and carbonates, are treated to recover potash, the potash being a valuable material for glass manufacture.

THE TRANSFORMATION FROM WOOD TO COAL.—As indicated previously, coal is of vegetable origin and has been converted into its present

form from trees and plants by the long continued and combined influence of temperature and pressure. The original dense vegetation has undergone a process of decay, and at various intervals in the earth's history has been covered up by clay, sand, etc., and hence subjected to pressure. The accumulation of earthy matter has also shut out air and arrested the decay. Since coal has been produced from vegetation, the two naturally contain the same elements, although the compounds into which these elements are formed are different in the two cases. The reactions by which vegetable fibre is converted into coal take centuries to accomplish, and we should expect to obtain material of a transitional nature between wood and coal. This is actually the case, and we can trace the transformation of the vegetation through fibrous to dense peat, to lignite or brown coal, and finally to the various qualities of coal proper.

During the slow transition from vegetation to coal, the principal changes that occur result in the elimination of moisture and of the gases carbon dioxide and methane. Both these gases are met with in coal mines, the carbon dioxide as "*black damp*," whilst the methane is the chief constituent of "*fire damp*." As this elimination of gases proceeds, oxygen is removed most quickly, next hydrogen, and the carbon most slowly; thus the proportion of carbon in the deposit gradually increases and that of the elements hydrogen and oxygen decreases. The mass becomes denser and harder, the final result being coal. The figures given in Table LXXI. serve to show the gradual change which occurs in the composition of the actual coal substance.

TABLE LXXI.—THE CHANGE IN COMPOSITION FROM WOOD TO COAL.

Substance.	Approximate Percentage Composition.		
	Carbon.	Hydrogen.	Oxygen and Nitrogen.
Wood fibre (dry)	50·0	6·0	44·0
Fibrous peat	52·0	5·8	42·2
Dense peat	59·5	5·7	34·8
Lignite	68·0	5·2	26·8
Lignituous coal	72·5	5·0	22·5
Bituminous coal	82·0	5·0	13·0
Semi-anthracite	88·0	4·7	7·3
Anthracite	94·5	2·5	3·0

The percentages of ash and moisture vary very considerably, the ash from 1 per cent. to 30 or even 50 per cent. in the case of peats and lignites, and the moisture from nothing up to 25 per cent. of the total weight of the coal.

(176) (B) PEAT.—Attempts have been made frequently to utilise peat as an industrial fuel, but with no great success. It may be an important fuel in the near future, especially for use in gas producers in conjunction with ammonia recovery plant. The chief problem in the

economic utilisation of peat as a fuel for direct firing consists of the removal of as much water as possible. When the peat is dried so as to contain about 25 per cent. of water it becomes usable in this way. On the other hand, it may be used in producers for gas-making with a moisture content as high as 60 per cent.

(177) (C) LIGNITE.—Lignite, or brown coal, is unimportant in the British Isles, but important deposits occur in Czecho-Slovakia, Germany, and other parts of Europe, India (one Assam deposit being 100 feet thick), Australia, and Canada. The deposit in Victoria,* Australia, equal in thickness to that in Assam, is being utilised for power production. The area of the lignite deposits in Canada is estimated at 60,000 square miles. Approximately one-third of the coal output of Germany and of New Zealand consists of brown coal.

The greatest uses for lignite are in gas-making with or without recovery of by-products, and for the manufacture of briquettes. The German Rhine deposits find considerable use in this way.

(178) (D) COAL.—The most important type of coal so far as the glass industry is concerned is the bituminous type. Bituminous coals generally burn with a yellow, luminous, smoky flame resembling that of the mineral bitumen, hence their name. There is no sharp line of demarcation between lignites and soft bituminous coals on the one hand, and bituminous coals and anthracite on the other. The main difference between the bituminous and anthracite types lies in the fact that the former give off a large quantity of combustible gas when heated out of contact with air, whilst anthracite coals contain very little volatile matter. The residue, after all volatile matter has been driven off, is coke, and, according to the character of this residue, bituminous coals are classified as caking or non-caking coals. These two classes may be further subdivided into *long-flame* and *short-flame* coals. Thus a long-flaming, non-caking coal may yield from 50 to 60 per cent. of coke, and at the other extremity, a short-flaming, "*semi-anthracite*," from 80 to 90 per cent. of coke, the remainder being volatile matter. The length and character of the flame depend largely upon the amount of volatile matter expelled from the coal when heated to about 1000° C. Only gases or vapours burn with a flame, and where a solid or liquid appears to burn with a flame it is because the substance is wholly or partially volatile at the temperature of combustion, and it is the volatilised portion which so burns. Flame may therefore be stated to be "*gas or vapour, which, at its surface of contact with air, is burning with the emission of light.*"

Anthracites or "*semi-anthracites*" are largely used for boiler firing, and form the class of fuels known as "*smokeless steam coals.*" Since these coals contain a very high percentage of carbon, they give off very little gas on heating out of contact with air, the volatile matter amounting to about 10 per cent. or less. Anthracite is hard and brittle, contains as a rule very little foreign matter, burns practically without flame or smoke, produces an intense heat locally, yields a very low percentage of ash, and is frequently burned under forced draught.

The particular variety of coal to be selected depends largely on the purpose for which it is required. For direct-fired furnaces, a long-

* J. Soc. Chem. Ind. 1919, 38, 350R.

flame coal is usually necessary. The firing of furnaces directly with coal is a wasteful process, and is rapidly being superseded by gas firing. The most suitable coal for coal-gas making is one which yields a fairly soft, porous, adherent coke and a high percentage of volatile matter. A non-caking coal producing a soft, porous coke which falls readily in the producer and does away with the necessity for constant poking is preferable for producer-gas making.

There are three other factors which determine the suitability of the coal—namely, the amounts of moisture, ash, and sulphur which it contains. All coal, when raised from the pit, contains water. On exposure in the air, much of this water is lost, and in the "air-dried" condition coal contains from 2 to 5 per cent. of water. It is almost impossible to determine by simple methods the amount of water in coal, since, on heating at 100° C., although the water is driven off, oxidation of the coal also occurs, partly counterbalancing the weight of moisture lost. Quite apart from moisture derived from the pit, water is picked up in the process of washing the coal. This applies particularly to the smaller sizes of coal, slack, pearls, peas, etc., which may, in bulk, contain over 10 per cent. of water.

TABLE LXXII.—GRÜNER'S CLASSIFICATION OF COALS.

Grüner's Names.	Equivalent Names.	Carbon.	Hydrogen.	Oxygen.	Ratio	Products of Distillation			
					Oxygen Hydrogen.	Ammonia Liquor.	Crude Tar.	Gas.	Coke.
Dry, long flame, non-coking	Non-caking, long flame	75 to 80	5.5 to 4.5	19.5 to 15.0	4	12 to 5	18 to 15	30 to 20	50 to 60
Fat, long flame	Gas	80 to 85	5.8 to 5.0	14.2 to 10.0	3	5 to 3	15 to 12	20 to 17	60 to 68
Fat, coking	Furnace	85 to 89	5.5 to 5.0	11.0 to 5.3	2	3 to 1	13 to 10	16 to 15	68 to 74
Fat, short flame	Caking	88 to 91	5.5 to 4.5	6.0 to 5.5	1	1	10 to 5	15 to 12	74 to 82
Lean coals	Anthracite	90 to 93	4.5 to 4.0	5.5 to 3.0	1	1 to 0	5 to 2	12 to 8	82 to 90

The ash in coal usually varies from 1 to 10 per cent., but, as already mentioned, may be considerably higher. The ash present in coal reduces its value as a fuel. The composition of this ash is important, for if it contains substances which are readily fusible, the formation of clinker

is almost inevitable, and this is detrimental in all heating methods where coal is used.

Sulphur may be present in coal up to about 3 per cent. The commonest form of occurrence is as iron sulphide (iron pyrites), FeS_2 . The ash of coal containing iron pyrites may be coloured red due to the formation of iron oxide, Fe_2O_3 , during combustion, the sulphur being burned to sulphur dioxide. This applies to the burning in air, for when the coal is heated out of contact with air, part of the sulphur remains in the coke and the remainder escapes as sulphuretted hydrogen, H_2S , or carbon disulphide, CS_2 , with the other gas evolved.

The other constituent of coal which is of any importance is nitrogen. Since some of this element, which may be present to the extent of about 1.5 per cent. of the coal, is evolved as ammonia, coals containing much nitrogen are most suitable for use in a plant for the recovery of nitrogenous products.

There are a number of classifications of coals, but that proposed by Gruner is probably the best and answers very well for practical purposes. It is based on the ultimate compositions of the coals, as shown in Table LXXII., on p. 235. The cokes which are obtained are of different types, a brief description of them being given in Table LXXIII.

TABLE LXXIII.—DESCRIPTION OF COKES FROM GRÜNER'S COALS.

<i>Coal.</i>	<i>Coke.</i>
Non-caking, long flame.	Powdery or only slightly adherent.
Gas.	Caked, soft, many crevices.
Furnace.	Caked, moderately compact.
Caking.	Caked, very compact, hard, lustrous.
Anthracite.	Powdery or only slightly adherent.

(179) **The Non-Caking, Long-Flame Coal** yields a large quantity of gas and leaves a coke which usually retains the form of the original lumps of coal. The coke is practically non-adherent. The volatile portion, usually about 35 per cent. of the coal, includes a large amount of tarry matter, and the coal burns with a long, smoky flame. The following is an average analysis of this type of coal:

Volatile hydrocarbons	36.0 per cent.
Coke	59.0 "
Fixed carbon	55.0 "
Ash	4.0 "
Sulphur	0.8 "
Moisture	4.2 "

The fixed carbon, mentioned above, is the residue left in the coke after deducting the percentage of ash, which is, of course, included in the coke.

(180) **Gas Coals** yield about 10,500 cubic feet of coal gas per ton. The coke is more adherent than that from the long-flame, non-caking

coal, but does not cake to any appreciable extent. As their name indicates, these coals are used mainly for gas-making, and have approximately the following composition:

Volatile hydrocarbons	31.0 per cent.
Coke	66.0 "
Fixed carbon	62.0 "
Ash	4.0 "
Sulphur	0.8 "
Moisture	2.2 "

(181) **Furnace Coals**, so-called, include the house coals, and they are the most generally useful. These coals cake and give a dense grey coke. Their approximate composition is—

Volatile hydrocarbons	27.5 per cent.
Coke	70.0 "
Fixed carbon	67.0 "
Ash	3.0 "
Sulphur	1.2 "
Moisture	1.3 "

(182) **Caking Coals** provide a solid, compact coke, and, though used in the same way as furnace coals for industrial and domestic purposes, they find most use in the making of coke, which may reach over 80 per cent. of the weight of the original coal. An average composition is—

Volatile hydrocarbons	21.0 per cent
Coke	75.0 "
Fixed carbon	71.0 "
Ash	4.0 "
Sulphur	1.2 "
Moisture	2.8 "

(183) **Anthracites** and most of the steam-coals burn with practically no smoke, owing to the small amount of volatile matter. The coke is practically non-adherent. The average composition is about—

Volatile hydrocarbons	7.0 per cent
Coke	90.0 "
Fixed carbon	87.0 "
Ash	3.0 "
Sulphur	0.5 "
Moisture	2.5 "

Various other forms of fuel are derived from coal by distillation—namely, coke, tar oil, and gas. The two last-named will be dealt with later.

(184) **(E) COKE**.—Coke has been mentioned already, and the various forms discussed under section (D). It is the residue left after bituminous coal has been heated out of contact with air and the volatile matter driven off. About 60 per cent. of the weight of the coal remains behind as coke. The coke from gas-making is used in the glass industry, but not the type obtained from coke ovens, which is employed primarily for metallurgical purposes. The most useful sphere for coke is found in the small producer-gas plants, where it forms a substitute for coal.

Gas coke, as mentioned above, varies considerably in composition. If the coal from which the coke is obtained contains a high percentage

of ash, then the coke also will contain a high percentage of ash. It follows that the average coke will contain a higher percentage of ash than the average coal, since all the ash in the coal remains behind. The ash in coke varies from 2 to 20 per cent. A good gas coke has the following composition approximately:

Carbon	89.0 per cent.
Hydrogen	0.5 "
Oxygen and nitrogen	2.5 "
Ash	8.0 "

(185) (F) **BRIQUETTES**.—Small coal or slack, often wasted on certain plants, has within recent years been utilised in block or briquette form. The fine coal may be cemented together by means of a number of materials, but pitch is generally used. In Germany, lignite has been extensively used in briquette form for producer-gas making. Peat may be similarly utilised.

Ordinary briquettes are rectangular in shape, weigh from 4 to 9 pounds, pack easily into a smaller space than an equivalent amount of coal, and their heating power is not far short of that of the coal from which they are made.

(186) **Liquid Fuels**.—(A) **NATURAL OILS**.—The natural oils which are used as fuels are usually termed petroleum oils. There are a number of varieties, and all may be used as fuel in furnace work except the type which, on distillation, yields such a variety of light oils that its value is too great to allow of its use generally as a fuel. This type of oil is that obtained mainly from the eastern States of America. The oils obtained from California, Texas, and the Black Sea-Caspian-Persia area are of types mostly used for fuel purposes.

Fuel oils of this nature vary from pale, limpid liquids to reddish-brown or jet-black oils of the consistency of treacle. In general, fuel oils contain about 85 per cent. of carbon and 15 per cent. of hydrogen, but, like coal, may contain small amounts of impurities such as sulphur, nitrogen, arsenic, phosphorus, and water. The analysis of Standard Grade Mex Fuel Oil is approximately as follows:

Carbon	83.52 per cent.
Hydrogen	11.68 "
Sulphur	3.27 "
Ash	0.16 "
Undetermined (oxygen, nitrogen, etc.)	1.37 "

The heating or calorific power of oil is about 50 per cent. greater than that of coal. In addition it is claimed that oil gives greater efficiency in use, needs less labour and storage room, has a greater uniformity of composition than coal, is cleaner in use, is convenient to handle, is more adaptable than solid fuel, and enables the temperature of a furnace to be controlled much more easily. Against such advantages must be placed the questions of relative cost, constancy of supply, and wear and tear of furnace refractories. The last-mentioned factors are variable and will be dealt with further in Chapter XXVIII. along with the methods of using oil fuel in glassworks.

(187) (B) **DISTILLED OILS**.—These may be obtained from the crude

petroleum oils previously mentioned, from oil-shales, from coal tar or blast-furnace tar.

When the petroleum oils are distilled, various portions are taken off separately, such as light petroleum, naphtha, and kerosene. The heavier portions, such as kerosene, remaining towards the end of the distillation, are those used as fuel oils. The distillation of coal tar gives a "*tar oil*" as one of the products, and this oil finds considerable use in the glass industry both for heating furnaces and, more frequently, for glory holes.

(188) **Gaseous Fuels.**—(A) **NATURAL GAS.**—For some forty years combustible gases given off from the earth in Pennsylvania have been largely used as fuel. The composition varies with the locality and with the season, for the quantity available for use is considerably less in winter than in summer. The gas consists almost entirely of methane and ethane, and not infrequently contains a small quantity of oil vapours. Natural gas from Pittsburg, Pa., gives the following average analysis:

Hydrogen	4.5 per cent.
Methane	83.0 "
Ethane	12.0 "
Nitrogen	0.5 "

Whilst admirable for use in gas engines, it has peculiarities which necessitate careful treatment when it is used for furnace heating. About 14 cubic feet of air are necessary for the complete combustion of 1 cubic foot of gas, and consequently the construction of satisfactory burners and furnace ports is rendered difficult. Since the gas is so high in methane content, regeneration is impossible; the regenerator would soon be blocked by the deposition of carbon produced by the decomposition of the gas.

(189) **The Gases produced from Coal.**—The types of gas produced from coal for fuel purposes vary according to the process adopted for obtaining the gas from the coal. They comprise three varieties—namely, (B) *coal gas*, (C) *coke-oven gas*, and (D) *producer gases*.

(B) **COAL GAS.**—When coal, particularly bituminous coal, is distilled in a closed retort, that is, out of contact with air, amongst other products, a mixture of gases is obtained known as coal or bench gas. The plant used for coal-gas manufacture is complex, but consists essentially of (a) fireclay retorts heated externally and provided with an exit tube for the gases produced; these retorts are charged with coal, hermetically sealed and heated to a high temperature to drive off the gas; (b) apparatus for cooling the gas, washing out the ammonia it contains, and condensing the tar which is one of the products of distillation; (c) purifiers for removing carbon dioxide and sulphur compounds from the gas; and (d) gas holders.

One ton of coal gives from 8,000 to 12,000 cubic feet of gas, which has approximately the following composition:

Hydrogen	45.0 per cent.
Carbon monoxide	8.0 "
Methane	35.0 "
Olefines such as ethylene	5.0 "
Nitrogen	5.0 "
Carbon dioxide	0.5 "
Oxygen	1.5 "

Coal-gas is therefore almost completely combustible, only the nitrogen (and traces of carbon dioxide and oxygen) being non-combustible. Though chiefly used for domestic heating and for lighting purposes, it finds numerous uses in industry. For various operations where the quantity used is comparatively small and where cost is not a very serious consideration, the use of coal-gas as a fuel is very successful. Many glass manufacturers prefer to heat their glory holes with town's gas (coal-gas), whilst it is also used for heating lehrs, kilns for stained glass, and for bench blowpipes.

(190) (C) COKE-OVEN GAS.—The gas from by-product coking plants is very similar to and not much inferior to many towns' gas supplies, and may, in the near future, become an important and convenient source of heat supply for industrial purposes.

(191) (D) PRODUCER GAS.—Since this form of gas is the main fuel used at the present time in the glass industry, it is dealt with in some detail in Chapter XIX.

CHAPTER XIX

PRODUCER GAS AND GAS PRODUCERS

(192) **Introduction.**—Firing by gas is a distinct advance on the direct application of coal for heating purposes, and producer gas is, in most cases, the cheapest fuel for glass factories.

The underlying principle in the manufacture of producer gas is the conversion of carbon into carbon monoxide, and hence producer gas is the product of incomplete combustion in the gas producer. Now the heat given out from a definite amount of fuel is the same whether it is produced by burning the fuel directly and completely or indirectly—that is, by first partially burning the fuel in the producer, and finally burning the gases so evolved. Since there must always be a loss of heat from the fuel in the producer itself, it follows that the efficiency attained in the combustion of the gas, and the advantages due to the ease of manipulation and convenience in use, must at least counterbalance this loss of heat. That this is the case in glass furnaces will be shown later in the section dealing with furnaces.

Three forms of producer gas are in common use, viz.:

- (1) *Air-gas* or *simple producer gas*, obtained by passing air through the mass of incandescent coal or coke;
- (2) *Water-gas*, produced by passing steam through the incandescent fuel; and
- (3) *Mixed producer gas*, obtained by the use of steam and air simultaneously.

The last named form is commonly comprehended by the term “producer gas,” but the two simpler gases will be dealt with first, since they afford a convenient introduction to the consideration of the reactions concerned in the production of the mixed gas.

(193) **Air-Gas or Simple Producer Gas.**—Although experiments had been made on the utilisation of gaseous fuels during the previous fifty years or so, it remained for **Bischof**, in 1839, to introduce the first separate producer for the manufacture of combustible gases. This producer, a diagram of which is shown in Fig. 69, was a simple, cylindrical, firebrick chamber (**D**) with a capacity of about 150 cubic feet. The fuel (which was peat in **Bischof**'s original producer) was fed in through the top, the space between the cover, **A**, and the sliding damper, **B**, being sufficient to hold the required amount of fuel for each charge. Since the cover, **A**, was closed down before the damper, **B**, was opened to allow the fuel to drop into the producer, no gas was allowed to escape on charging. The fuel rested on the grate, **F**, to a depth of seven or seven and a half feet.

Air was admitted through openings in the door, **H**, of the ashpit, **J**. The size of the openings could be altered at will, and the amount of air admitted to the fuel regulated by this means. The air was drawn in simply by chimney draught operating through the furnace which the producer was intended to supply. Through the door, **G**, the grate could be cleaned whilst the fuel in the body of the producer was poked through holes, **E**, in the side, these holes also serving for observation of the condition of the contents of the producer. The gases were removed by a side outlet, **C**, above the top of the fuel bed. It is interesting to note that the principal features of this producer are embodied in the majority of producers to-day.

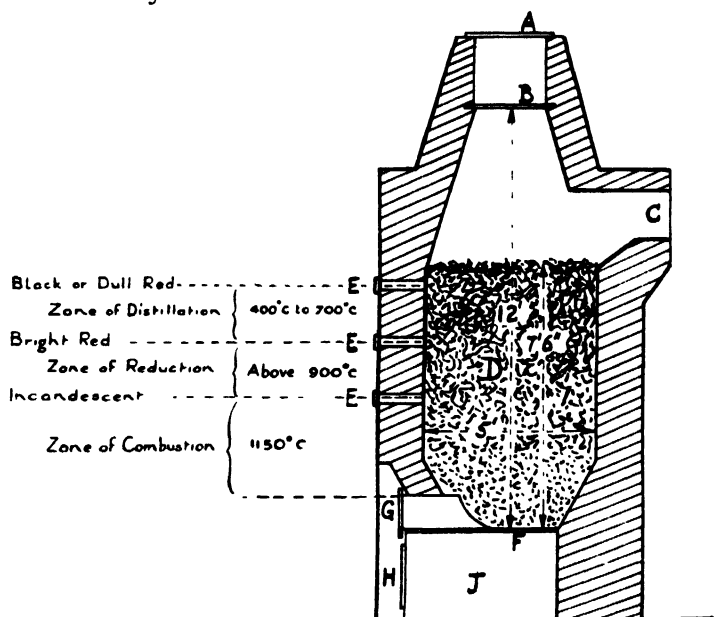


FIG. 69.—THE BISCHOF PRODUCER.

The first producer which proved to be a commercial success was invented by **F. Siemens** in 1857 in connection with a regenerative furnace. This producer (see Fig. 70) consists of a chamber, **B**, rectangular in cross-section, one side, **F**, of which is inclined at an angle of from 45° to 60° . A grate, **E**, is provided at the foot of this inclined side. The fuel is filled in at **A**, and falls in a thick bed upon the grate. The air for combustion is drawn through the grate by chimney draught as in the Bischof producer, and the gases formed pass out at **C**.

The reactions which take place in simple producers of the Bischof or Siemens types result in a gaseous fuel containing about 30 to 35 per cent. of combustible gas. In the lower part of the fuel-bed the air passing in produces a layer of incandescent coke, and near the grate the carbon of the fuel burns to carbon dioxide, as represented by the following equation:



Further up in the fuel bed the quantity of oxygen available for combustion is limited, and consequently carbon monoxide is produced as indicated in equation (2):



Another reaction also occurs, however, as the carbon dioxide passes upwards through the glowing fuel-bed. The red or white hot coke reacts

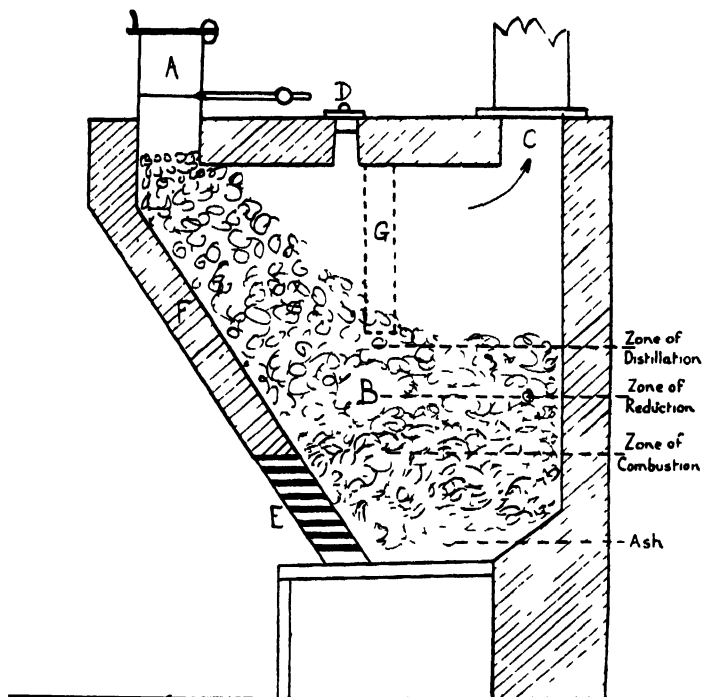
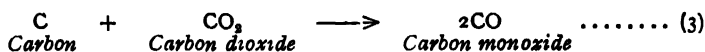
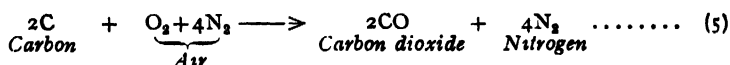


FIG. 70.—THE SIEMENS PRODUCER.

with the carbon dioxide already formed, and reduces it, producing carbon monoxide, the desired product for burning, as shown in equation (3):



Since air, and not oxygen, is used in the producer, equations (1) and (2) may be better expressed thus:



Accordingly, as the producer continues in operation, a mixture consisting principally of nitrogen from the air and carbon monoxide from the fuel will pass towards the exit of the producer. If the fuel used be coke, this mixture of gases forms the product of the operation; but if bituminous coal is used, the fuel in the upper part of the producer undergoes partial distillation out of air due to the heat from the actively burning fuel below it. As a consequence, a certain amount of coal-gas and tarry vapours enrich the gas formed in the lower part of the producer and pass with them into the furnace. Siemens gives the following analysis by volume of producer gas made in 1865 in the glassworks of St. Gobain in France, the fuel used being a mixture of three parts caking coal and one part non-caking coal, and the producer having water under the grate:

Carbon monoxide	23.7 per cent.
Hydrogen	8.0 "
Methane	2.2 "
Carbon dioxide	4.1 "
Oxygen	0.4 "
Nitrogen	61.5 "
						—
						99.9 "

Thus, when coal is used in making producer gas, the bed of fuel may be divided roughly into three sections: the portion near the grate, where the carbon is almost completely burned to carbon dioxide, may be termed the "*zone of combustion*"; the centre portion, where the carbon monoxide is produced from the carbon dioxide, may be termed the "*zone of reduction*"; whilst the upper portion, where the coal-gas, etc., are produced, may be conveniently called the "*zone of distillation*."

When carbon is converted to gas in a producer such as has been described, about 30 per cent. of the heat units available in the fuel are liberated in the producer, and if the gases issuing from the producer are cooled to ordinary temperature, then only 70 per cent. of the heating units of the fuel can be obtained when the gases are burned in the furnace. However, it is not necessary that all the heat liberated in the producer shall be lost, because the gases leave the fuel-bed at a temperature ranging from 400° C. to 900° C., and if this heat from the burnt fuel, carried by the gases, be utilised by burning the gas whilst it is still hot, then from 85 to 90 per cent. of the available heat units in the fuel may be conveyed to, and utilised in, the furnace.

The amount of heat produced by the burning of the fuel in the producer depends on the rate of combustion, which is chiefly determined by the ease of access of air to the fuel and the velocity of the air, carried by the "pull" of the chimney, through the fuel-bed. The temperature of the air-gas producer rises until the rate of production of heat is counterbalanced by the rate of loss of heat in the gases, ashes, and in other ways. It is obvious that in certain cases the temperature might rise sufficiently high to cause combustion throughout the whole fuel bed if the air supply were excessive, but the practical limit of temperature is reached when trouble arises due to clinker (fusing of the ash) and fusing of the refractory lining of the producer. With the Siemens producer as described, however, the fuel bed is so deep that the resistance it offers

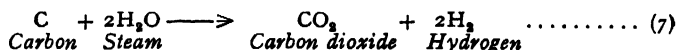
to the passage of air and gas is very considerable, and the working of the producer, by chimney draught, is comparatively slow. The rate of working can be increased by enclosing the grate and introducing air under pressure, but troubles due to clinkering of the ash render this method of increased working of no special advantage.

The temperature of the producer is therefore kept within limits by introducing steam. Not only does the steam keep the producer temperature from rising too high, but, by reacting with the carbon, actually adds carbon monoxide and hydrogen to the producer gases, and that without introducing nitrogen. The gas produced by the action of steam on red-hot carbon is termed "steam-gas," or more commonly "water-gas."

(194) **Water-Gas.**—If the fuel, coal or coke, be raised to a high temperature by an air blast and then steam be passed in, a reaction represented by the following equation occurs:



Whereas the reactions between carbon and oxygen give out heat in the producer, the reaction represented by equation (6) absorbs heat and consequently cools the fuel-bed. Whilst the fuel bed remains at a temperature above about 900°C ., the reaction between steam and carbon proceeds almost entirely as indicated in equation (6), but as the temperature falls below 900°C . another reaction, represented by equation (7), asserts itself:



This action also absorbs heat, but less in proportion to the amount of carbon consumed than that indicated by equation (6). It follows, then, that the further the temperature of the fuel falls, the greater will be the percentage of carbon dioxide in the gas produced. A point is finally reached where the gas produced by the steam-carbon reaction is quite inefficient, and, at the same time, steam passes through the fuel bed unchanged. It is then necessary to cut off the steam and reheat the fuel by again using air.

This alternate decomposition of the fuel by air and steam is made use of for the manufacture of "blue water-gas." The air-gas produced by the "air-blow" is used for heating purposes on the plant, particularly for superheating the steam, and the "water-gas" produced by the "steam run" finds its chief use in gasworks for mixing with ordinary coal-gas for incandescent lighting. Though the heating power of water-gas is not much more than half that of coal-gas the temperature of the water-gas flame is greater than that of the coal-gas flame, and hence its value for the purpose mentioned. The gas can be obtained with over 90 per cent. of combustible gases, as the following analysis of an unpurified sample shows:

Carbon monoxide	43.0	per cent.
Hydrogen	48.0	"
Methane	0.5	"
Carbon dioxide	3.0	"
Nitrogen	5.5	"

The intermittent nature of water-gas production renders storage in gas-holders necessary, and as, for furnace purposes, this is impracticable, a mixture of air and steam is used in the producer.

(195) **Air-Steam Producer Gas.**—It has already been noted that when steam is introduced into the fuel bed it cools the producer and also adds carbon monoxide and hydrogen to the gas. Since steam, unlike air, does not introduce the non-combustible nitrogen, its use increases the proportion of combustible material in the producer gas, and the temperature which can be obtained by burning the gases in the furnace is correspondingly higher. Steam, therefore, affords a ready means of controlling the producer temperature and avoiding clinkering and other troubles incidental to high temperature in the producer, and also of yielding a gas of increased heating value compared with simple producer gas. The amount of steam which can be used with the air is, as already mentioned, strictly limited, but by adjusting the relative proportions of air and steam, a temperature balance can be maintained in the producer and a definite composition of the air-steam gas obtained. In most modern producer gas plants, air, saturated with steam, is blown into the producer. The hotter the air, the more steam will be required to saturate it, and in practice it is found that if the air blown into the producer is saturated with steam at a temperature of about 50° to 55° C., the best results are obtained, as regards a gas for glass furnace work. Such a gas would be termed a "steam enriched" producer gas.

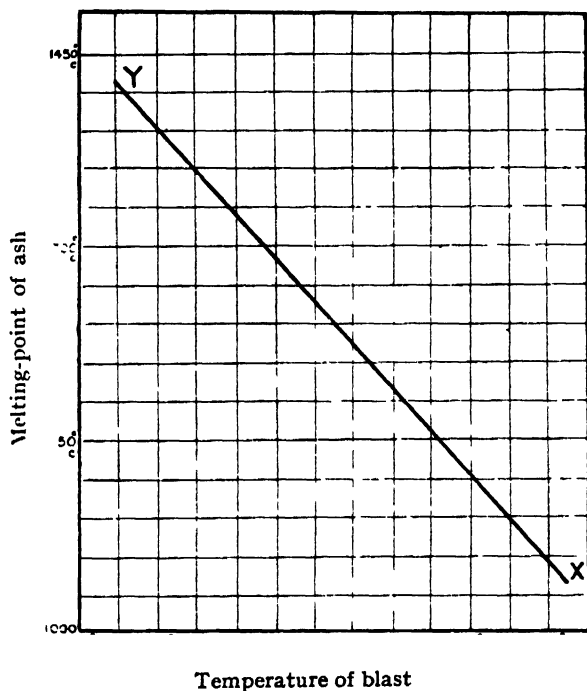
To regulate the amount of steam used in a jet-blown producer, or in producers where steam is otherwise introduced into the pipe providing the air supply, a thermometer should be used to determine the temperature of the steam-air mixture passing to the producer. If the air is not preheated, a temperature of 60° C. in the steam-air mixture indicates that there are present 80 per cent. of air and 20 per cent. of water vapour by volume. This temperature should not be exceeded unless the ash of the fuel is very fusible, since the proportions of air and steam indicated bring the working temperature of the producer to a point at which undecomposed steam begins to pass through the fuel bed. The temperature in the "zone of combustion" should never fall below 1125° C. When the ash of the fuel fuses below that temperature the temperature of the producer must be reduced accordingly, but, as a result, the producer works less efficiently.

A. L. Culbertson* states that, by experimenting with many different kinds of coal, the melting-point of the ash has been found to vary from 1040° C. to 1430° C. Corresponding to these temperatures the blast temperature necessary to prevent clinkering in the producer varies from 65° C. to 42° C. A straight line (see Fig. 71) drawn between these two points gives the temperature of the blast for any temperature of the "zone of combustion" in the producer. The line is straight since the temperature of the zone varies inversely as the amount of steam decomposed, which again varies directly with the temperature of the blast.

Theoretically, one pound of carbon at a high temperature will decompose completely about two-thirds of a pound of steam. The amount of steam to be used per pound of fuel cannot be set at any definite figure

* Engineer, Chapman Engineering Co., Mt. Vernon, Ohio.

to suit all producers, all fuels, or all methods of working. It is not uncommon to find more than a pound of steam being used per pound of coal gasified when a clinkering coal is used in a fixed grate producer. This large quantity of steam used tends to give a moist gas which has distinct disadvantages. It is possible to have a consumption of not more than a third of a pound of steam per pound of fuel gasified even with a clinkering coal where the type of producer and method of working generally are suitable for such a fuel. With preheated air and superheated steam a much larger proportion of steam can be used. The



$$(x = 65^\circ \times 1040^\circ; y = 42^\circ \times 1430^\circ.)$$

FIG. 71 —BLAST TEMPERATURE CHART.

(By courtesy of Messrs. Stein and Atkinson, Ltd., London)

most economical proportion of steam is not easily determined, and depends on the type of producer, the character of the fuel, the nature of the air supply, the temperature of the steam, and the depth of the fuel bed. The steam used should be dry so as to avoid excessive cooling. Superheating is a distinct advantage, and is done in some cases by passing through a deep ash-bed or round an annular space in the lower part of the producer. The fuel depth need not exceed three feet six inches. When the fuel depth exceeds this, the frictional resistance offered by the fuel to the passage of the blast and the gases is such as to reduce the rate of gasification. A deeper fuel-bed is necessary when a caking coal is used which tends to cause "chimneys" or "air-channels"

through the fuel-bed. On the other hand, too thin a fuel bed tends to cause incandescence throughout, with the result that much carbon dioxide may pass through undecomposed. Reduction of the blast causes a decreased rate of gasification, whilst a slight increase in the depth of the fuel-bed may reduce the carbon dioxide without materially affecting the rate of gasification.

All modern gas producers use air and steam together, and in the following pages the development of the air-steam blown gas producer will be briefly traced. Various improvements have been made in the original Siemens type of producer from time to time. Thus by closing up the ash-pit by means of air-tight doors, and introducing a jet of steam below the bars, a steam enriched gas could be produced. This is sometimes accomplished also by having a shallow trough of water under the grate. The water is evaporated by heat radiated from the grate and the steam drawn up through the fuel by chimney draught. Further, by forcing the gas distilled from the fuel to pass through the incandescent coke before mixing with the producer gas, the tarry matter can be converted into simpler gases which can be burnt in the furnace. This is effected by having a partition reaching down into the fuel from the top of the producer between the top of the fuel-bed and the gas exit, as shown at **G** in Fig. 70.

Though Siemens' fuel-bed was deep for chimney draught it was comparatively shallow when used with a blast, and as a result much steam and carbon dioxide passed through the fuel undecomposed. A differently arranged fuel bed was therefore necessary, and many variations of such a steam-jet, forced-draught producer have been constructed and successfully used.

The air is now generally introduced into the producer some distance above the bottom, and a thick layer of ashes accumulates, upon which the weight of the fuel rests.

(196) **The Brook-Wilson Producer.**—In 1876 Brook and Wilson introduced such a producer (see Fig. 72), having a solid bottom and no firebars. The air and steam were introduced through openings in the side of a hollow ridge of brickwork, **A**, running across the bottom of the producer. The gas exits, **B**, were so arranged that the products of distillation of the fresh fuel were forced through the red hot fuel below before they were drawn off from the annular flue as shown at **C**.

The cleaning out of ashes from this producer, and others of a similar type, about every twelve hours was a laborious undertaking, and necessitated the cutting off of the steam blast and hence the stoppage of the producer. Although this work was accomplished expeditiously in most cases, it was considered most necessary to avoid, if possible, the periodical short stoppages of the working of the producer. Wilson then brought forward a modification of his producer in which the air and steam were introduced at a higher level and the ashes were removed by means of two large archimedean screws, each of which cleaned half the producer. In order to keep the screws cool and prevent their rapid corrosion it was found necessary to fill the producer bottom with water, which also served as a seal to prevent escape of gas.

Solid bottom producers, though still used in many places, have been

largely replaced by water-sealed ones. In this type of producer the ashes and clinkers, which form the bed on which the fuel rests, are received in a vessel of water so arranged as to seal up the bottom of the producer hermetically and prevent escape of gas. Since the ashes are received into water, they are quenched and the heat contained in them returned to the producer in the form of steam. Further, as the bottom of the producer is comparatively cool, there is not the same tendency to form clinkers, and the removal of the ashes is considerably facilitated.

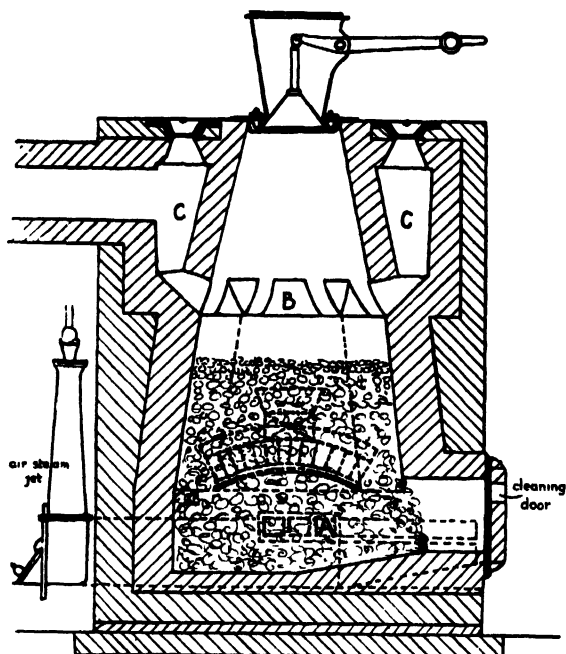


FIG. 72 —THE BROOK AND WILSON PRODUCER.

(197) **The Duff Producer.**—The Duff producer (see Fig. 73) consists of a square or rectangular* chamber in a cylindrical casing. The air and steam are blown in through a ridge, made up of transverse, inclined grids, across the bottom of the producer. The fuel is charged in intermittently, and the ashes, which slip off the inclined grates, are removed periodically from the water trough which seals the bottom of the producer. The settling of the fuel is aided by poking through holes in the producer side. The distinct advantage in this producer at the time it was introduced was that no stoppage was required in order to remove ashes. Duff producers, or modifications, are working in many plants at the present time.

(198) **Revolving Grate Producers.**—Many improvements have followed the introduction of the water seal, the improvements being mainly con-

* Certain modern variations are cylindrical.

cerned with the feeding of the fuel, the avoidance of clinkering, the use of inferior coals, and the removal of the ashes. One of the chief methods adopted for avoiding clinkering and removing ashes is by means of a revolving grate. The Duff and Wilson producers suffer disadvantages due to the fluctuation of quality and quantity of the gas produced caused by intermittent charging and removal of the ashes. Automatic feeding of the fuel not only increases and renders more uniform the quantity and quality of the gas, but also saves labour in connection with coal handling equipment and increases the furnace output. Revolving grate producers are almost entirely fitted with automatic feeding devices, but even in small installations of stationary producers such devices are advantageous.

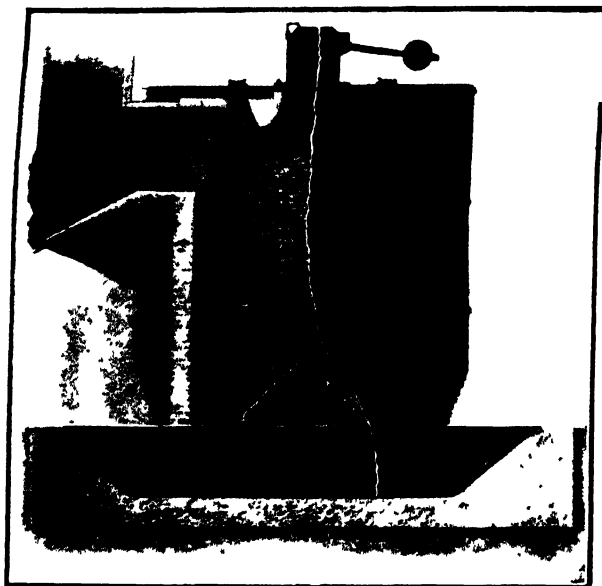


FIG 73—THE DUFF PRODUCER

(By courtesy of the H. L. Dixon Co., Pittsburg, Pa.)

It is often claimed for the revolving grate type of producer that it will gasify practically any kind of fuel, including highly caking coals. However, to avoid possible disappointment in connection with this claim it is better to refrain from using in a producer any coal which readily cakes. These producers are, in the main, suitable for fuels with high ash contents. Where a fuel with high ash is used in a fixed grate producer a great deal of strenuous labour is required for the removal of the ashes, and, accordingly, automatic ash removal is a distinct advantage. This removal may be intermittent or continuous. When intermittent, say once or twice every twenty-four hours, the fuel-bed and the gas produced cannot be so constant in character as when the ash removal is continuous.

The speed of revolution of the ash-basin largely determines the depth of the ash bed, and must be regulated to suit the ash content of the fuel. Ordinarily, from four to eight revolutions per twenty-four hours are required, but with coals having an ash content of over 10 per cent., one revolution per hour may be necessary.

Semi-automatic or automatic producers cost very considerably more to instal than the stationary type, and are more expensive generally in running. The advantages already indicated, however, can, under suitable producer control, effect economies which save the additional cost.

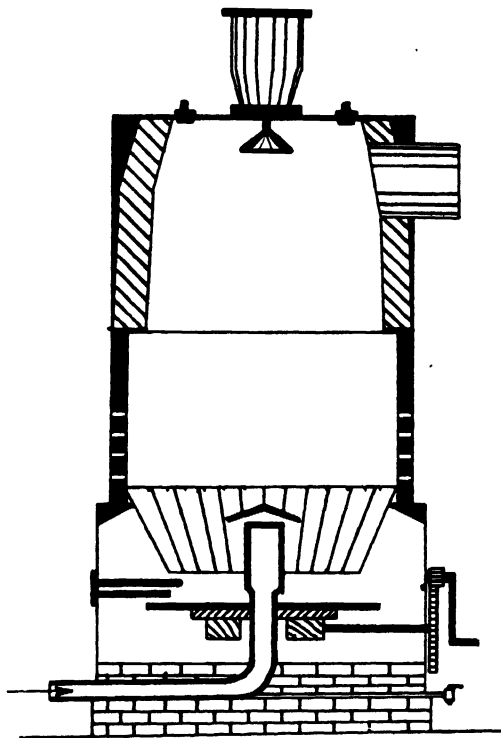


FIG. 74.—THE TAYLOR PRODUCER.

(199) **The Taylor Producer.**—The W. J. Taylor gas producer is one of the early revolving grate types without a water seal. It is cylindrical, lined with firebrick mainly, but in some cases a metal water jacket forms the lower part of the body. With a coal which is liable to clinkering this is a distinct advantage, in that clinker will not adhere so readily to the smooth, cooler sides of a water jacket as it will to a firebrick lining. In the form illustrated in Fig. 74, the coal, in dropping into the producer, passes through a distributor which scatters the fuel and tends to spread it evenly over the bed. The air and steam are blown in through a central vertical pipe. The end of this pipe (*tuyere* or *twyer*) is covered by a

mushroom-shaped hood, as is the case in nearly all centre-blown producers, in order to prevent fuel or clinker blocking the opening, and also to increase the area of action of the air-steam blast. This producer carries a deep fuel-bed on a large quantity of ashes. The revolving bottom imparts a twisting or grinding action in the lower part of the fuel-bed and tends to close up any channels, formed by the blast, through which steam and carbon dioxide might pass unchanged to the exit from the producer. By turning a wheel a few times at frequent intervals the fuel-bed is consolidated and the ash discharged mechanically by a shovel.

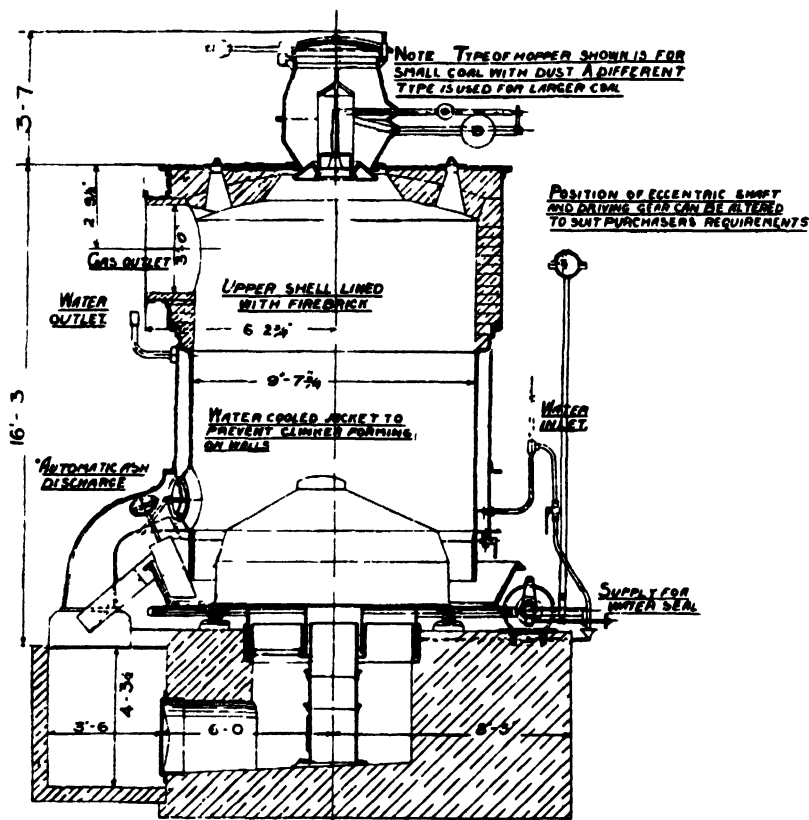


FIG. 75.—THE KERPELY PRODUCER
(By courtesy of Messrs. L. G. Appleby and Co., Ltd., London)

(200) **The Kerpely Producer.**—A producer adopting similar methods to the Taylor is the well-known Kerpely producer. This producer has, however, a "wet-bottom" or water seal. It is primarily designed to allow a high rate of working without clinkering and to facilitate the removal of ash. A revolving grate (see Fig. 75), of a polygonal shape, with an eccentric cone built up of a series of flat shelves between which the air

and steam are blown into the producer, brings to bear a torsional strain on the ash and fuel bed, breaking up the clinkers before they attain any size. The ashes fall into a water-trough, whence they are automatically discharged as they come up against fixed iron shovels. The bottom portion of the producer, where the most active chemical action occurs, is not built of brick but of hollow water boxes forming a water-cooled jacket. This, as in the Taylor producer, is intended to keep the producer body cool and prevent adhesion of clinker. Owing to the corrosive action of clinker on the metal, which is produced by the rotation of the eccentric cone, the water-cooled jacket must be made of special steel. The gas is taken off at the side through dust catchers before reaching the gas main. In the ordinary Kerpely producer the coal is fed by a bell-hopper arrangement, and mechanical means are generally used for carrying fuel to the hoppers.

To compensate for the increased cost as compared with the ordinary solid-bottom producer it is claimed that the Kerpely producer ensures the maximum gasification capacity per square foot of grate area, the complete control of the fuel-bed, uniform combustion in the fuel-bed, minimum labour in poking and in the removal of ash, and the production of a uniformly good quality of gas from any fuel. It is only fair to say that these claims are probably justified when the producers are under skilled control.

For instance, with a coal of the following analysis—

Fixed carbon	42.03 per cent.
Volatile hydrocarbons	23.65 ..
Sulphur	2.42 ..
Ash	23.90 ..
Moisture	8.00 ..

the average compositions of the gases obtained from a fixed grate producer and from a Kerpely revolving grate producer were as given in Table LXXIV., the advantage being distinctly on the side of the latter.

TABLE LXXIV.—A COMPARISON OF PRODUCER GASES.

<i>Gas, Etc.</i>	<i>Fixed Grate Producer.</i>	<i>Kerpely Producer.</i>
	<i>Per Cent.</i>	<i>Per Cent.</i>
Carbon dioxide	11.00	2.94
Carbon monoxide	17.50	25.42
Hydrogen	9.00	8.86
Methane	2.75	3.26
Total combustible gases ..	29.25	37.54
Moisture in grams per cubic metre	46.5	33.60

(201) **The Morgan Producer.**—Another producer using a water seal and automatic ash and clinker removal is the Morgan producer. The makers of this producer, in order to ensure uniformity of quality and a high heating efficiency of the gas, endeavour to maintain their working conditions as uniform as possible—that is the depth of the fire, the

removal of ash, and the prevention of adhesion of clinker to the producer lining. This producer (see Fig. 76) is circular in section and tapers slightly from the middle to the base. The air and steam in the desired proportion are driven into the producer through the pipe, **A**, and are distributed evenly throughout the fuel-bed by means of the mushroom cap, **B**. As in the Taylor producer, when the mixture of air and steam is forced through the hot ashes, it abstracts heat from them which would otherwise be wasted. The producer is usually fed by an automatic feeding arrangement, the one shown in Fig. 76 being the **George feed**. This feed distributes the fuel regularly and evenly over the fuel bed. The advantages of this will be obvious; not only is the fuel bed kept at a constant depth, but since fresh fuel is continually falling into the producer the amount of coal-gas distilled off is regular and the producer

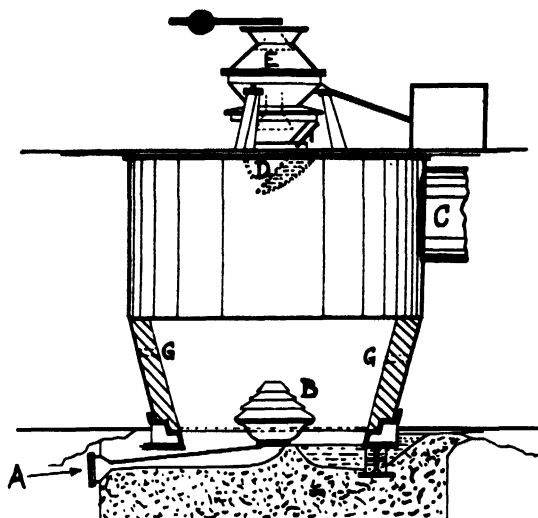


FIG. 76.—THE MORGAN PRODUCER.

(By courtesy of the International Construction Co., Ltd., London.)

gas, drawn off at **C**, is always of even quality. The George feed consists of an inclined feeding spout, **D**, cooled by water, which is kept continually, but very slowly, rotating. The fuel is charged into the feeding hopper, **E**, and regularly forced out of this hopper into the rotating feeding spout, **D**, by means of a revolving disc. Openings in the wall of the producer, at **G**, serve for observation, or poking if necessary. A revolving grate automatically discharges the ashes from the water seal.

(202) **Automatic Producers.**—The producers previously described all require a certain amount of hand poking. The shearing effect on the ash bed, brought about by the revolving bottom, is generally insufficient to ensure complete uniformity of the fuel-bed and entire absence of channels. A number of producers have been designed to overcome this difficulty, also embodying further improvements or modifications with the intention of increasing general efficiency.

The Talbot Producer.—One of the earliest types of mechanical producer is the Talbot producer (see Fig. 77). The bottom of the producer is fixed, with a water seal. The upper part of the blast mushroom forms a bearing for a vertical, water-cooled shaft down the centre line of the producer, to which two or more water-cooled stirring arms are attached. The shaft is revolved by mechanism on the charging platform, and the arms stir the fuel in the producer. This agitation of the fuel is rendered more complete by combined rotary and vertical movements of the shaft. Though these movements are somewhat elastic, the stirrer is difficult to keep in order, arms break, particularly the lower ones, so that in the latest design the lower arms are dispensed with.

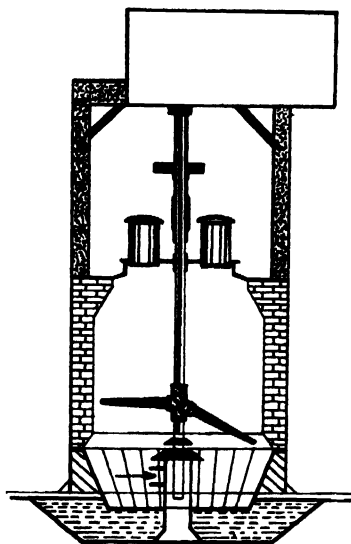


FIG. 77 —THE TALBOT PRODUCER.

(203) **The Kerpely Producer (with Agitators).**—To the Kerpely producer has been added what is known as the **Bentley system** of mechanical feeding and poking (see Fig. 78). The producer is of the general type already described. The mechanical feed is easily adjustable, even whilst working, to any rate of feeding. The fuel is delivered on to a conically shaped fuel spreader, and so is evenly distributed. Mechanical pokers, water-cooled, are used, two being of the curved type and two having T-heads. The curved pokers stir the fuel and prevent accumulations of clinker, whilst the shorter T-pokers level and spread the fuel and break up caking lumps.

It is interesting to compare the analysis of the gas obtained from the ordinary Kerpely revolving grate producer (see Table LXXIV.) with the analyses given in Table LXXV. of gas from a mechanical Kerpely producer with pokers, etc.

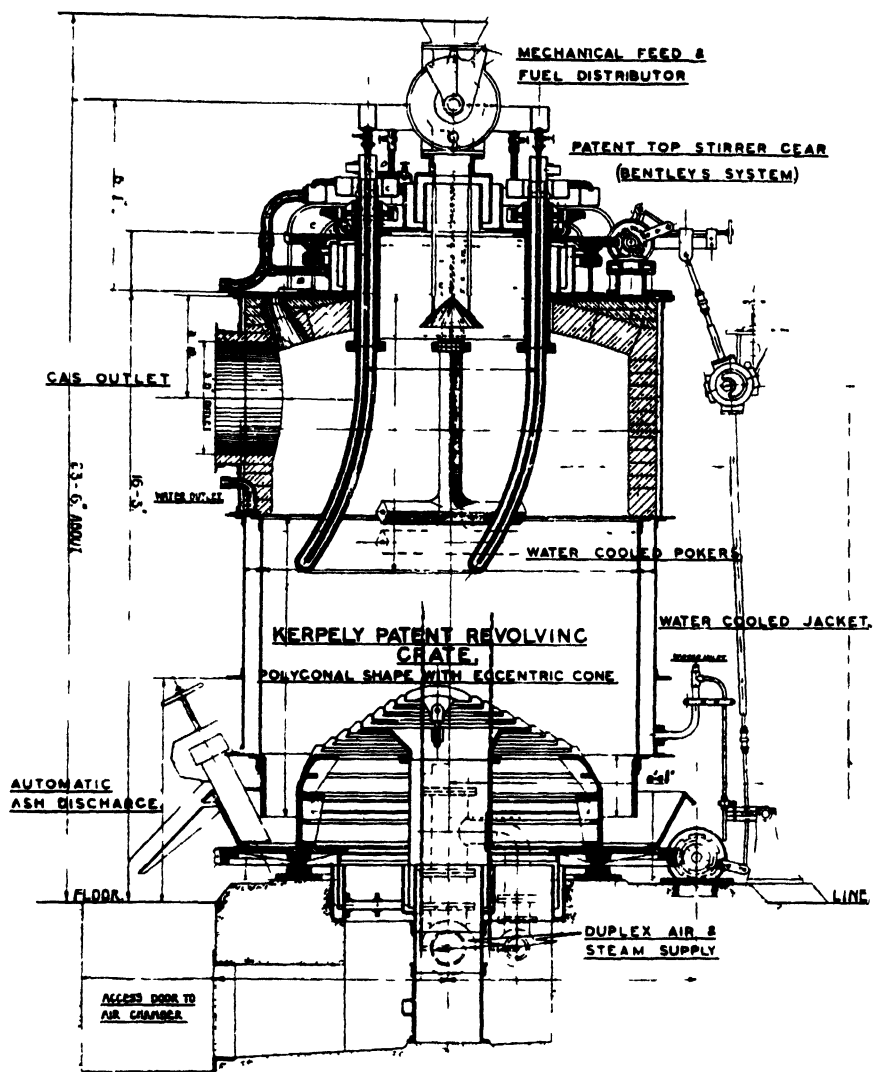


FIG. 78.—THE KERPELY PRODUCER (WITH MECHANICAL POKERS)
(By courtesy of Messrs E G. Appleby and Co, Ltd, London)

(204) **The R. D. Wood Producer.**—The R. D. Wood producer (see Fig. 79) has a shell which is divided into a stationary upper portion and a revolving lower portion, the latter carrying the conical bosh or ash pan, so that the fuel-bed will revolve with the shell. Two pokers also rotate at such a speed that their lower ends describe a path as shown in Fig. 80. The shell completes two rotations per hour. Ash

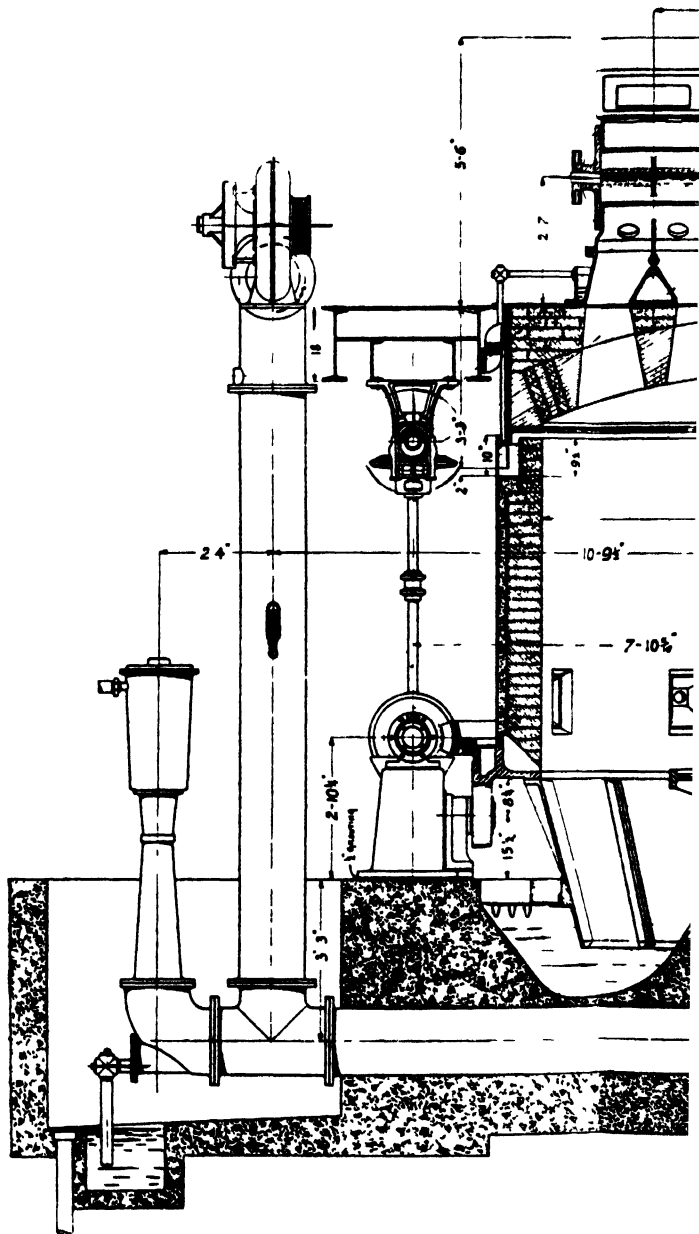


FIG. 79—THE R. D. WOOD
(By courtesy of the H. L. Iron Co.,

is removed continuously by a plough attached to the lower edge of the producer wall and reaching into the ash-bed.

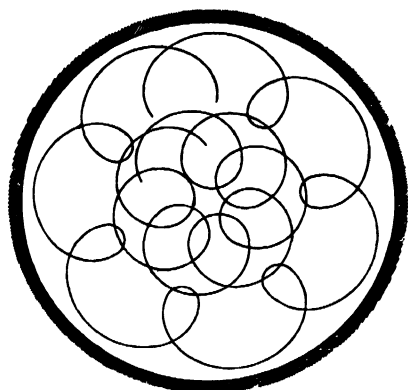


FIG. 80.—PATH OF POKERS IN THE R. D. WOOD PRODUCER.
(By courtesy of the H. L. Dixon Co., Pittsburg, Pa.)

It is claimed that this producer with a diameter of 10 feet 6 inches will do the work of four ordinary hand-poked producers and costs no more. In addition there is a much greater efficiency and uniformity obtained, and remarkable records have been secured in America with it.

TABLE LXXV.—PERCENTAGE COMPOSITION OF KERPELY PRODUCER GAS.

Date.		CO ₂ .	CO.	CH ₄ .	H ₂ .	N ₂ .	Total Combustible Gases.	Blast Saturation Temperature.
								Degrees C.
Dec. 19, 1921	..	5.0	24.3	3.77	14.47	52.46	42.54	58
" 20 "	..	3.6	26.4	4.17	13.07	52.76	43.64	61
" 21 "	..	4.0	27.4	3.65	13.26	51.69	44.31	54
" 22 "	..	3.1	28.3	4.14	14.48	49.98	46.92	57
" 23 "	..	3.6	28.8	3.15	14.42	50.03	46.37	58
" 24 "	..	3.0	29.2	3.16	14.14	50.50	46.50	59
" 28 "	..	3.8	26.2	4.20	15.19	50.61	45.59	58
" 29 "	..	4.8	26.4	3.69	12.65	52.46	42.74	55.5
" 30 "	..	3.4	27.4	4.14	14.72	50.34	46.26	57
Jan. 2, 1922	..	5.0	25.0	4.20	14.00	51.80	43.20	56
" 3 "	..	5.4	25.4	3.68	14.68	51.24	43.76	57
" 4 "	..	4.0	26.0	3.71	13.37	52.92	43.08	56
" 5 "	..	3.2	28.6	4.16	13.32	50.72	46.08	57
" 6 "	..	3.6	28.0	4.10	13.68	50.62	45.78	58

(205) **The Wellman Producer.**—The Wellman mechanical producer (the original type of which was installed by W. B. Hughes at Pencoyd Iron Works in 1897) may rightly claim to be the most popular mechanical

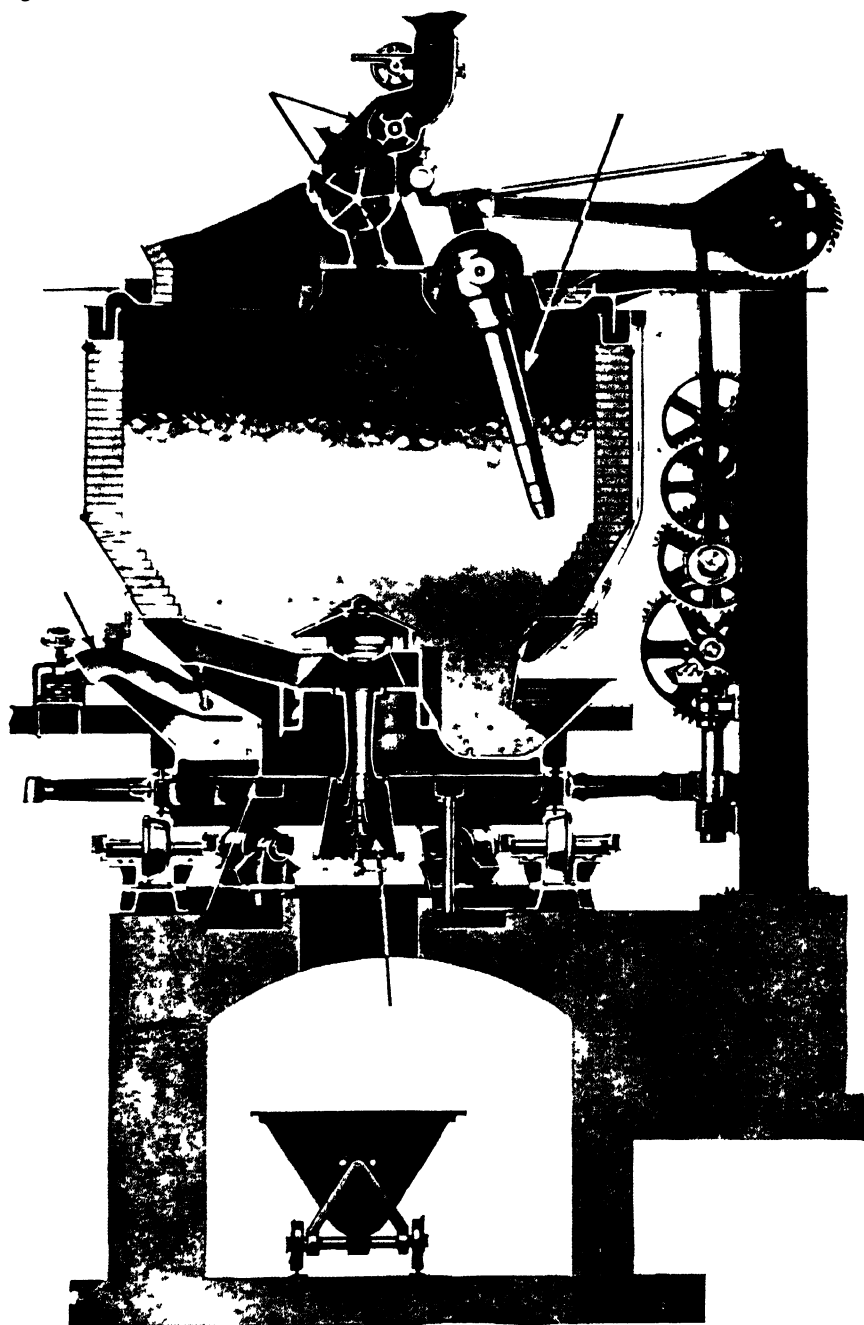


FIG 81 —THE WELLMAN PRODUCER

(By courtesy of the Wellman, Smith, Owen Engineering Corporation, Ltd , London)

producer in America. The type shown in Fig. 81 is a considerable advance on the original Hughes producer. It has a double automatic feed and a poker. The poker moves to and fro in a vertical plane, whilst the lower part of the producer shell revolves with the fuel as in the case of the R. D. Wood producer. The poker is water-cooled, penetrates into the incandescent zone, and its path is a series of loops as shown in Fig. 82. The producer makes seven or eight revolutions per hour, and the ash is removed once or twice every 24 hours by a bar which is inserted above the revolving grate and held stationary.

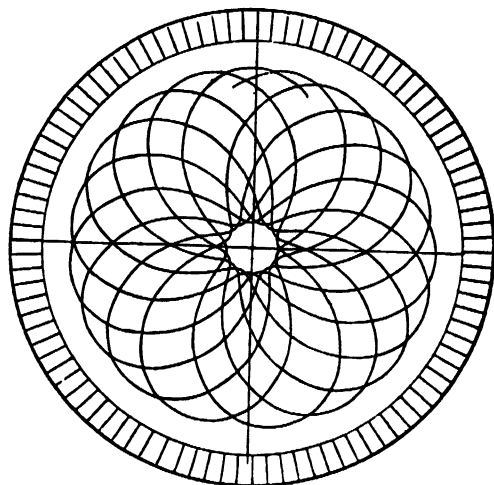


FIG. 82.—PATH OF THE POKER DURING TWELVE REVOLUTIONS OF THE WELLMAN PRODUCER.

(By courtesy of the Wellman, Smith, Owen Engineering Corporation, Ltd., London.)

(206) **The Morgan Gas Machine.**—One of the most modern gas producers, illustrated in Fig. 83, is the Morgan producer gas machine. The makers of this producer deny that any agitation of the fuel bed is necessary, but consider that “*if the coal is properly spread and the surface continually levelled, all that the fire needs is to be left alone. Other disturbance causes variations of density which create hot places, and consequently poor gas and clinkers.*” The coal is fed automatically into the producer direct from an overhead bin at frequent intervals and levelled by the U-tube roller, **B**, which floats on the fuel and permits any practical variation in height of the fuel-bed. The blast is delivered from three hollow, radial arms, **A**, and around the whole circumference of the hollow ring or mantle. There is therefore a gently sustained pressure distributed evenly in the fuel-bed. The firebrick lining of the producer is comparatively thin and water-cooled, **B**, to prevent attachment of clinkers. The walls and ashpan revolve about five times per hour, carrying the fire-bed round with them. A suitable spiral-shaped bar or plough, **C**, is fitted in the revolving ashpan and sweeps the entire producer bottom automatically, causing a uniform settling of ash. By setting

lever **D** the plough can be held stationary during one revolution of the ashpan and then automatically released. During this period the ash is

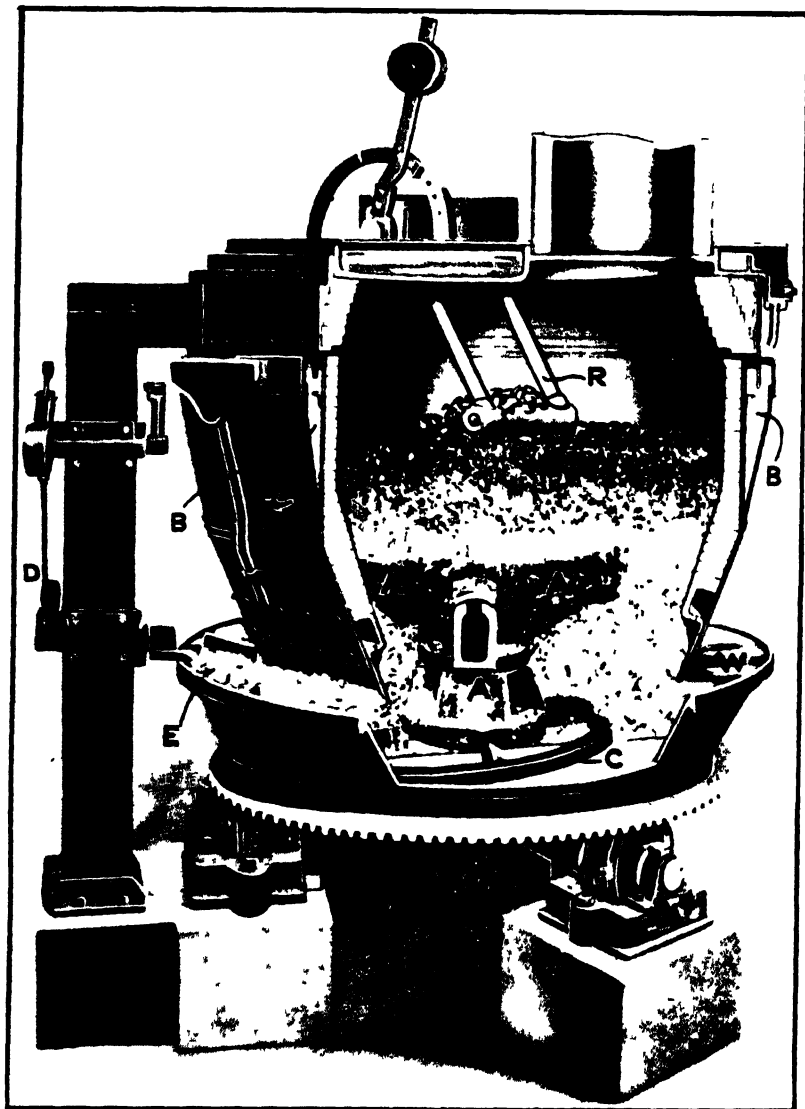


FIG. 83.—THE MORGAN GAS MACHINE.

(By courtesy of the International Construction Co., Ltd., London.)

discharged from the water seal, **W**, at one point, **E** (see also Fig. 84), and is practically free from carbon. The fuel-bed may be assisted in

settling after ash removal by hand poking, otherwise the machine dispenses with manual labour. The ashpan is supported on three wheels, **F**, each 24 inches in diameter, on dust-proof bearings, and the power required to drive the whole is 0.75 horse-power. This power is doubled



FIG 84.—ASH DISCHARGE ON THE MORGAN GAS MACHINE.

(By courtesy of the International Construction Co., Ltd., London.)

for the short period during ash removal. Such a producer, 10 feet in diameter, will gasify over 3,000 pounds of coal per hour without in any way decreasing the heating value of the gas. Works tests prove the efficiency of this machine in practice over considerable periods whilst giving a gas of the following average composition:

Carbon monoxide	28.8 per cent.
Hydrogen	11.9 "
Hydrocarbons	.	.	3.5 "
Carbon dioxide	.	.	3.5 "
Nitrogen, etc	52.3 "

A photograph of an installation of Morgan gas machines is reproduced in Fig. 85. The feed and roller mechanism, and the gas exit tubes are clearly shown.



FIG 85 —THE MORGAN GAS MACHINE (CHARGING PLATFORM)
(By courtesy of the International Construction Co, Ltd, London)

(207) **The Chapman "Agitator."**—A feature which can be fitted to any producer to prevent the need for any excessive poking is the Chapman agitator. Fig. 86 shows a producer fitted with Chapman automatic feed and agitator. This agitator combines poker-stirring with rolling as just dealt with. It is not fixed, but has the vertical shaft fitted with a special driving head having two large screw-like spiral flanges. Should the agitator strike an obstruction or become covered too deeply with fuel, thus requiring more power to rotate, it automatically screws up so that the working forces and depth of penetration into the fuel-bed are brought back to their original adjustment. Consequently this stirrer is termed a "floating" agitator. The stirring fingers project forward

and plough up the fuel to a depth of from 8 to 14 inches, whilst the cross arm, following the fingers, closes up gaps in the fuel-bed made by the

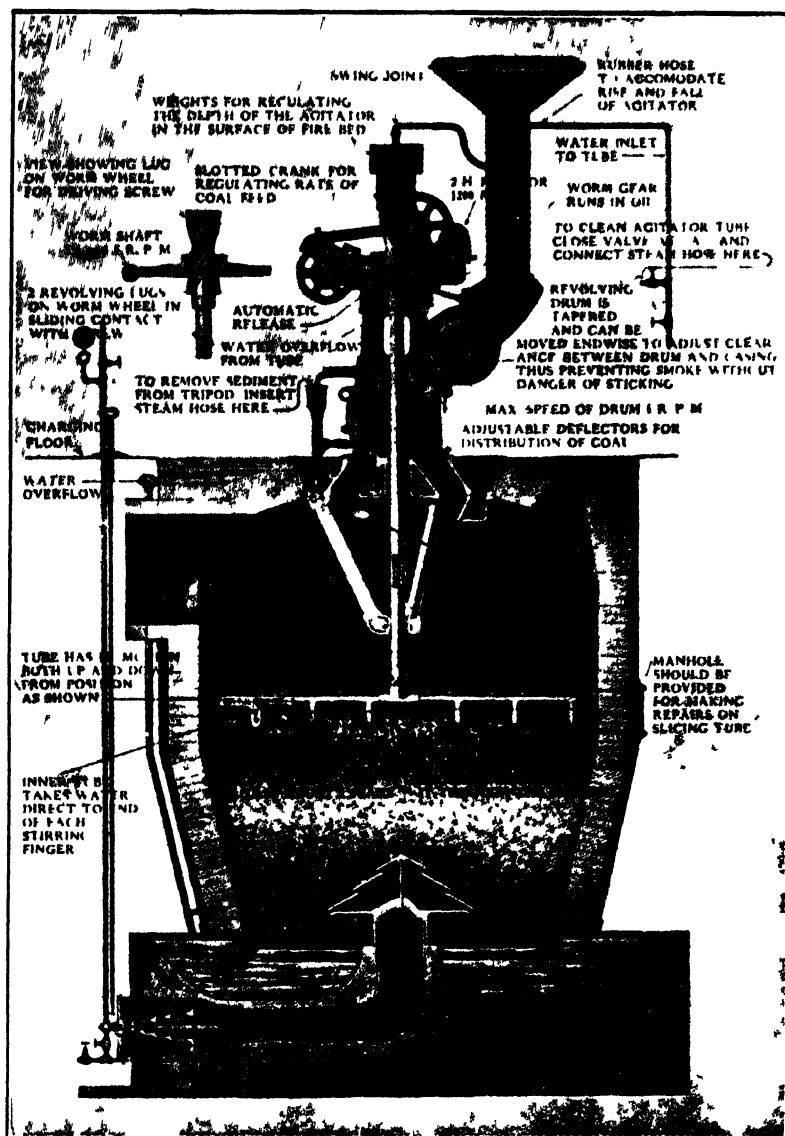


FIG. 86 —THE CHAPMAN AGITATOR.

(By courtesy of Messrs. Stern and Atkinson, Ltd., London.)

fingers. This prevents blow-holes and tends to stop dust from entering the flues. The agitator is not so liable to breakage as a comparatively rigid poker, but instead of breaking clinkers, like the Talbot poker,

would ride over them. It is claimed, of course, that the agitator prevents clinkers and that slack coal may be used in a producer fitted with the device to advantage. The agitator is water-cooled throughout, and the complete Chapman producer includes an automatic feed as shown in Fig. 86, and also a device for automatically and continuously removing the ash. Since this producer may have diameter of 11 feet (larger than any other mechanical producer) its capacity is increased accordingly. The agitator revolves once every seven minutes, and therefore each part of the upper fuel-bed is disturbed every three and a half minutes.

The value of the agitator when fitted to other producers is demonstrated by the following figures quoted from a reprint* of a paper by W. B. Chapman.

"A Duff producer, operating originally at 10 tons a day and making gas having 125 B.T.U., was fitted with a Chapman agitator and automatic feed, and at 36 tons a day gave an average of 163 B.T.U. Similarly, a Von Kerpely producer, the most popular mechanical type in Europe, gasifying 20 pounds per square foot per hour, making about 135 B.T.U. gas, was equipped with Chapman agitator and automatic feed and changed to 34 pounds gasified per square foot per hour and 178 B.T.U. This was maintained without difficulty and without any hand poking."

(208) **The Efficiency of a Gas Producer.**—A certain amount of recapitulation is necessary in considering producer efficiency. It has already been mentioned that the heat given out from a definite amount of fuel is the same whether burned directly on a grate or indirectly by first gasifying the fuel and burning the gases. Since the object of the producer is to furnish gas by the use of which heat can be generated, it follows that the greater the amount of heat lost from the fuel in the producer the less will be the amount of heat obtained from the gas produced. Producer gas as a fuel can only be more economical in use than solid fuel when the greater efficiency attained in general by the use of the gas more than counterbalances the loss of heat during the gasification of the solid fuel in the producer.

There are many ways in which heat may be lost in a gas producer. It is lost by radiation into the atmosphere, is carried out in the ashes, clinkers, combustible gases, and in any carbon dioxide or water vapour in the gases. All these losses should therefore be reduced to a minimum. The heat lost by radiation can be minimised by efficient lining and lagging of the producer. Loss in the ashes, often due to a defective grate, is comparatively small, and is least in water-bottom producers where the heat is utilised in volatilising water. However, if the ashes, owing to improper working of the producer, contain unburnt carbon, potential heat energy is lost, and, as the amount increases, such loss may seriously affect the efficiency of the producer.

All producer gas contains some carbon dioxide, but the amount should not exceed 4.5 per cent. If the amount exceeds this percentage, either the fuel-bed is not deep enough or the temperature of the "zone of reduction" is not sufficiently high to decompose all the carbon dioxide passing through it from the "zone of combustion." The use of excess steam will increase the proportions of carbon dioxide, hydrogen, and

* *Glass Industry*, 1921, 2, 290.

water vapour in the gases, and reduce the proportion of carbon monoxide. The use of a fuel with caking tendencies or one having a readily fusible ash, the attempt to run the producer at too great a speed, resulting in a very high temperature, or inefficient poking, may all result in the formation of blow-holes or chimneys owing to the clinkering of the fuel. These channels are bad, because not only do they give rise to considerable local heating, but they allow carbon dioxide, and even air and steam, to pass through the fuel-bed. Carbon dioxide may also be present in excess owing to the burning of carbon monoxide in the gases caused by the presence of oxygen above the fuel-bed. This is derived from any air passing up channels in the fuel-bed or from a leakage of air into the producer from outside. As carbon dioxide is already completely oxidised it has no heating value.

Notwithstanding minimisation of these losses, a certain amount of the total heat available in the fuel must be utilised in order to produce the gas. The gas issues from the producer at a temperature usually over 400°C ., and consequently contains "sensible" heat due to its temperature, besides the heat obtainable on subsequent burning. If the gas is used in the furnace whilst hot, as much as 85 per cent. of the heating value of the solid fuel used is available in the furnace. With certain modern producers it is claimed that the amount may reach 93 per cent. This percentage of heat available when the gases are hot is known as the "hot-gas efficiency."

In many plants, however, the gas is allowed to cool before use. Then the "sensible" heat is lost in dust catchers, gas mains, etc., and only the heat produced by the burning of the gas is available. The percentage of the total heating value of the solid fuel available in the cold gas (below 100°C .) is termed the "cold-gas efficiency." In furnaces using regenerators, the "cold-gas efficiency" is the more important (see Chapter XXVI). Too high a temperature in the gases is frequently due to insufficient supply of fuel or steam, or to the ash-bed being too thin.

The efficiency of a producer must obviously depend very largely on the mode of construction and working. For the best results to be obtained there should be a constant feed of fuel of the correct size, the rate of feeding being readily controlled; an even distribution of fuel should be made over the whole of the fuel-bed, so that no thin places may occur which might lead to the development of hot spots; there should be thorough poking or agitation, particularly of the upper layers of fuel, in order to obtain a compact and even fuel-bed; and correct adjustment of temperature in the producer by proper and easy control and distribution of the proportions of air and steam is necessary. All these conditions are met, more or less, by the Talbot, Wood, Wellman, Morgan, Kerpely, and Chapman producers.

The size of fuel is important. Small lumps give ready access of air with large surface of contact, and nuts, 0.75 to 2.5 inches in diameter, are best for producers. Dust should be avoided, since it increases the tendency to clinkering and, with agitation of the fuel, will be carried out of the producer into the gas lines. Failing the use of dust-catchers, the dust may then reach the furnace itself. This is a very serious consideration in glass furnace practice, and the use of washed coal presents a distinct advantage.

The greater the tendency to caking, the greater should be the depth of the fuel-bed owing to the liability to form channels, but greater depth leads to a reduced rate of gasification. With an average fuel the ashes should be maintained at a level of 10 to 14 inches above the tuyère. The "combustion" and "reduction" zones should total 6 to 20 inches in thickness and be covered by a layer of more or less raw fuel some 12 to 18 inches in depth.

The most suitable air pressure, steam-saturation, depth of ash-bed, speed of grate revolution, etc., must be found for each fuel by repeated trial, and analysis of the gas produced. As the tendency to clinkering increases the greater must be the amount of steam used. The saturation temperature of the air blast usually varies from 42° C. to 65° C., according to the nature of the fuel, and the temperature of the combustion zone should not fall below 1125° C. for efficient working. With the fuel depths specified above, a steam pressure of from 20 to 30 pounds will be necessary.

Hand-poked, hand-fed producers, with a diameter of 8 feet to 10 feet, will gasify from 900 to 1,000 pounds of coal per hour, semi-automatic producers, of similar size, up to 2,500 pounds, and automatic producers from 3,000 to 3,300 pounds.

Even in the best regulated factories "accidents will happen," and the producer plant, of whatever type, should have a capacity of at least 25 per cent. above the estimated average requirements. The choice of type must obviously depend on local conditions as regards capacity required, fuel and labour available, and, in the case of high-grade producers, technical knowledge and equipment.

(209) **The Advantages of Gaseous Fuels.**—1. Whereas with solid fuels, a very much larger amount of air must be supplied than is theoretically necessary for the combustion of the fuel a very slight excess is sufficient in the case of gaseous fuels. This is very important when we consider that all the excess air requires to be heated up to the temperature of the furnace and leaves it at a very high temperature, thus carrying away with it a large amount of heat.

2. The heat in the exit gases can be recovered to a large extent and used to heat both gas and air previous to combustion.

3. The gas is burnt, and the heat produced, in the furnace itself, precisely where required, and not, as is frequently the case with solid fuels, in a fire-box separated from the heating chamber.

4. The atmosphere of the furnace—that is the supply of gas and air—is under better control, and the conditions may be made oxidising or reducing as desired.

5. Owing to the preheating of gas and air, higher temperatures may be attained.

6. There is greater convenience and economy in manipulating the fuel. The gas producers may be erected at any point on the works and the gas distributed as required by pipes. Thus the fuel can all be dealt with on one spot and does not require carting to each separate furnace. This results in greater cleanliness and freedom from dust.

7. Lower grade fuels, such as could not possibly be used for direct firing, may be employed.

CHAPTER XX

REFRACTORY MATERIALS

(210) **Introduction.**—It is almost impossible to over-estimate the importance of refractory materials in the glass industry. On the quality of the refractories employed depend, in great measure, the life of the furnace, the amount of fuel used, and the quality of the ware produced. Inferior refractories may cause grave losses in the glass factory, and it is essential that the glass manufacturer should thoroughly understand the nature and the quality of the material which would best serve his interests, and also that the maker of refractory articles should be able and willing to produce materials of the required standard.

Refractory materials are those which are used in the construction of furnaces, flues, pots, etc., or used as tools, on account of their resistance to heat when they are subjected to the chemical and cutting action of dust and gases, the action of the glass and glass-making materials, sudden changes of temperature, to blows and strains, to tension, and particularly to compression. Either high or low heat conductivity may be required, whilst the rate of expansion or contraction should be uniform within conveniently narrow limits. Capability to be formed into shapes easily is also generally necessary, and the material should be capable of being readily procured and treated.

The choice of the material depends on the nature of the substances or the chemical conditions to which the refractory may be exposed and the temperature at which it is to be used. The requirements of refractories for glass furnaces are comparatively modest as regards temperature, about 1450° C. being the maximum except in very special cases. In attempting to meet this and other requirements, regard has to be paid to both the chemical and physical characteristics of the material: (a) *chemical*, because the fusibility and reactivity depend on composition; (b) *physical*, because density, porosity, heat conductivity, expansion or contraction with change of temperature, and mechanical strength will depend largely on physical condition.

In the glass industry there are several types of refractory materials employed. Metals such as iron, steel, platinum, and aluminium are used; non-metallic elements such as carbon in the form of graphite or charcoal for moulds; also wood for flint workers' tools, and for moulds as used by French sheet glass blowers. In use, the surface of the wooden articles becomes rapidly carbonised. The compounds used include such materials as sand or silica, and fireclays. A definite relationship is necessary between the molten substance or substances and the containing vessels

or tools used. Since glass is rather acid in character it would never do to use a container of basic material such as lime or magnesite, because there is always a tendency for combination between acidic and basic oxides. Instead, an acidic substance, usually containing much silica, is used, such as firestone or fireclay. Materials from the batch are volatile, especially the alkalis. The latter will readily act on the silica crowns in tank furnaces. In closed pots the roof of the pot is of fireclay and therefore distinctly less acidic. On a furnace with open pots the cost of repairs to the furnace is always greater than when closed pots are used, owing to the volatility of the materials. Even glass itself is not sufficiently acid to be allowed in contact with highly siliceous bodies such as silica bricks, since these are rapidly attacked and disintegrated. Fireclays, strictly speaking, are neither acid nor basic materials, although many contain so much silica as to be classified as acid.

It is customary to classify refractory materials in three different groups, thus—

- I. Neutral refractories.
- II. Basic refractories.
- III. Acid refractories.

(211) **Neutral Refractories.**—Metals such as iron and steel are used for blowing pipes or “irons,” various cutting and shaping tools, and for moulds. Platinum is necessary for analytical and other chemical operations up to quite high temperatures connected with glass-making and is very difficult to replace. Non-metals like carbon in the form of charcoal, coke, graphite, coal, burnt sawdust and cork dust also find considerable employment. Graphite is used largely for metallurgical crucibles. Occasionally it is used in the making up of clay for glass pots, but may cause discolouration of the glass. It is non-plastic and needs mixing with plastic material before it can be made into shapes. Graphite is specially useful since it is less readily combustible than other forms of carbonaceous matter. Accordingly it is used in finely powdered form on the inner surface of moulds for spun, blown ware such as electric bulbs or chemical ware beakers and flasks.

Chromite, or chrome iron ore, $\text{Cr}_2\text{O}_3 \cdot \text{FeO}$, is made into bricks by mixing with lime or kaolin. Good chromite should contain more than 40 per cent. of chromic oxide, Cr_2O_3 , and less than 6 per cent. of silica. Its chief value lies in that it is scarcely affected by either slags or silica and in its refractoriness. Pure chromite has a melting-point of about $2180^\circ \text{C}.$ * Ground chromite makes a good mortar for high temperature (*e.g.*, electric) furnaces when mixed with dolomite. It finds little use, however, in glassworks.

(212) **Carborundum.**—Carborundum or crystalline silicon carbide, SiC , was accidentally discovered by E. G. Acheson in 1891, and is produced in the electric furnace by the partial fusion of a mixture of silica and carbon in the absence of air and then cooling the product somewhat slowly to promote crystallisation. The nature of the product formed depends on the conditions of manufacture.

* C. W. KANOLT (*Trans. Amer. Cer. Soc.*, 1913, 15, 167).

Crystalline carborundum forms at $1840^{\circ} \pm 30^{\circ}$ C.* and dissociates into its elements at $2240^{\circ} \pm 5^{\circ}$ C.,* the silicon volatilising and the carbon remaining as graphite. No fusion or softening occurs below the dissociation temperature.

In addition to crystalline carborundum there is the amorphous form termed by Acheson *siloxicon* ($\text{Si}_2\text{C}_3\text{O}$) and carbofrax. Together with the high decomposition point and lack of softening below decomposition, the following properties are claimed for carborundum refractories—extreme hardness and resistance to mechanical erosion, high thermal conductivity, low coefficient of expansion, high mechanical strength under heat conditions, no after-contraction or after-expansion, and great resistance to impinging gas and oil flames.

According to Pratt,† carborundum is harder than corundum, No. 9 in Moh's scale of hardness, and the use of the crystalline variety as an abrasive is well known. At 435° C. carborundum transmits 117 per cent. more heat than silica.‡ The thermal conductivities of certain refractories as determined by Wologdine§ at 1000° C. and expressed in gram-calories per cubic centimetre per degree centigrade per second are given as carborundum brick 0.0231, magnesia brick 0.0071, chrome brick 0.0057, clay brick 0.0042, and silica brick 0.0020.

The tables of the International Congress of Applied Chemistry, 1910, give for the coefficient of expansion of carborundum the following figures:

From	15° to 100° C.	-6.58×10^{-6}
"	700° „ 800° C.	-4.38×10^{-6}
"	800° „ 900° C.	-2.98×10^{-6}
At	$1000^{\circ} \pm 15^{\circ}$ C.	-4.35×10^{-6}

whilst C. A. Boeck|| gives for recrystallised carborundum, 4.74×10^{-6} at 100° C. to 900° C. Hodsman and Cobb,¶ using the commercial material bonded with a little clay, found that its expansion was continuous between 15° C. and 1000° C., as shown in Fig. 87, the mean coefficient of expansion between those temperatures, of a specimen previously fired at cone 9 for 72 hours, being 4.71×10^{-6} . No change in its rate of expansion was found by Houldsworth and Cobb** as the result of firing for two hours at cone 15 in the laboratory. After firing for two hours at 1550° C. to 1580° C. its expansion was somewhat less than before this treatment, but was still quite regular.

In order to adapt carborundum to its various uses the tensile strength of the bonded articles may be made to vary between wide limits. In ceramic bonded articles, where the bond does not introduce objectionable physical or chemical properties, a tensile strength of 1,400 pounds per square inch may be attained. A sacrifice of resistance to heat changes and chemical actions affecting ceramic articles must be expected when high tensile strength is desired. Articles of recrystallised carborundum may be made with a tensile strength of 1500 to 2000 pounds per square inch.

* SAUNDERS (*Trans. Amer. Electrochem. Soc.*, 1912).

† *Mineral Industry*, 1906, 15, 98.

‡ F. A. J. FITZGERALD (*Chem. and Met. Eng.*, 1912, 10, 129).

§ *Electrochem. and Met. Ind.*, 1909, 7, 383. || *Trans. Amer. Cer. Soc.*, 1912, 41, 477.

¶ *J. Soc. Glass Tech.*, 1919, 8, 201. ** *Ibid.*, 1921, 5, 16.

M. L. Hartmann and W. A. Koehler* have determined the transverse breaking strength of ten commercial refractory bricks at 20° C. and at

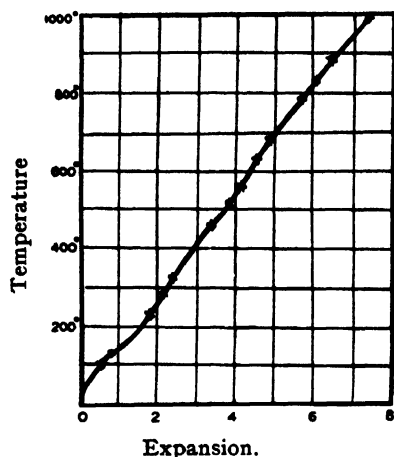


FIG. 87.—THE EXPANSION OF CARBORUNDUM.

1350° C. All the materials except two specimens of bonded carborundum showed a great reduction in strength at the higher temperature. The values obtained are quoted in Table LXXVI.

TABLE LXXVI.—BREAKING STRENGTHS OF COMMERCIAL CARBORUNDUM AND OTHER BRICKS.

Refractory.	Modulus of Rupture in Pounds per Square Inch.	
	(20° C.)	(1350° C.)
Carbofrax A	2,103	2,274
Carbofrax B	2,651	2,129
Carbofrax C	2,215	1,918
Silica No. 1	608	145
Silica No. 2	491	178
Magnesia	1,388	136
Fireclay Grade A	665	113
Bauxite	1,315	99
Chrome	1,392	22

Carborundum† is decomposed by fused sodium carbonate, fused alkaline sulphates, fused borax, and fused cryolite; is also attacked by sodium silicate at 1300° and by lime and magnesia at 1000° C. It is obvious, therefore, that carborundum refractories cannot be used in places where actual contact with common glass-making materials at high temperatures may occur.

* *Trans. Amer. Electrochem. Soc.*, 1921, 129.

† BARADUC-MULLER, *Rev. Mét.*, February, 1909.

Amongst the suggested uses for carborundum refractories is the construction of recuperators and regenerators. The prime fault in recuperators is leakage. The low coefficient of expansion and high density of carborundum bricks permit the construction of solid structures with no contraction or expansion tending to produce cracks or apertures for heat or gas leakage. Carborundum bricks are practically indestructible when subjected to changes in temperature, whilst the specific gravity of silicon carbide varies from 3·1 to 3·2 and the apparent density of refractory forms from 2·1 to 2·5. The high thermal conductivity of carborundum products renders them eminently suitable for partition walls in recuperators. Tubes made from carborundum have been successfully used in recuperators for experimental furnaces,* and a pot-arch accommodating 36-inch pots, used in the Department of Glass Technology, University of Sheffield, utilises carborundum tubes in this fashion. For muffle furnaces and indirect heating furnaces of all types carborundum refractories are supreme.

When used in furnaces they develop a brown siliceous glaze due to reaction between the silicon carbide and the binder, which largely prevents any subsequent decomposing action of furnace gases.

A finely powdered form mixed with from 5 to 10 per cent. of kaolin and made up into a cream can be painted on new furnace walls or on the outside of pots, and it lends much greater resistance towards heat and the erosive action of dust and flame.

Two main forms of refractory brick are made—†REFRAX (dense mass of carborundum crystals held together by recrystallisation at 2100° C.), and †CARBOFRAX (pure silicon carbide crystals bonded with a small amount of refractory clay). Their properties are summarised in Table LXXVII.

TABLE LXXVII.—PROPERTIES OF CARBORUNDUM REFRACTORIES.

<i>Property.</i>	<i>Refrax.</i>	<i>Carbofrax.</i>
Composition	98 to 99 per cent. SiC	—
Specific gravity	3·18	—
Apparent density	2·30	—
Porosity	28 per cent.	—
Weight (9" × 4½" × 3")	8·5 to 9 pounds	9·25 pounds
Tensile strength	1,000 to 2,000 pounds per square inch	1,000 pounds per square inch
Crushing strength	12,500 pounds per square inch	14,500 pounds per square inch
Specific heat (23° C.)	0·180	0·180
Thermal conductivity (100° C.)	0·0275	0·0243
Specific electrical resistance (25° C.)	50 ohms per c.c.	28,400 ohms per c.c.
Specific electrical resistance (1400° C.)	0·65 " "	40 " "

(213) **Zirconia.**—Zirconia, ZrO_2 , a high-grade refractory which has come into prominence during the last few years, instead of being regarded

* ROSENHAIN and COAD-PRYOR, *Engineering*, 1919, 107, 702.

† The terms "REFRAX" and "CARBOFRAX" are registered trade marks in this country of the Carborundum Co., Ltd.

as a rare oxide, is now one of the chief export products of Brazil. The oxide, zirconia, was first obtained in 1789 by Klaproth from Ceylon zircon, which is now known to consist of zirconium silicate. The substance occurs mainly in two forms, *baddeleyite* and *zirkite*. Baddeleyite is an impure form of the oxide containing from 70 to over 90 per cent. of zirconia, while zirkite is a mixture of zircon ($\text{ZrO}_2 \cdot \text{SiO}_2$) and baddeleyite and contains a similar proportion of zirconium oxide. The first named mineral, occurring in glassy lumps or nodules, was discovered in 1892 by Hussak in South Brazil and by L. Fletcher* in Ceylon. Zircon is also found in North Carolina, Florida, and South Norway.

In Table LXXVIII. are given two analyses of specimens of baddeleyite and some analyses of zirkite.

TABLE LXXVIII.—PERCENTAGE COMPOSITIONS OF BADDELEYITE AND ZIRKITE.

Mineral.	ZrO ₂ .	SiO ₂ .	Fe ₂ O ₃ .	Al ₂ O ₃ .	TiO ₂ .	MnO.	CaO.	MgO.	H ₂ O.	Loss on Ignition.	Total.
Baddeleyite (a)†	84.10	7.74	3.10	0.66	1.21	—	—	—	—	2.72	99.53
„ (b)‡	74.72	13.16	3.50	1.10	1.00	—	2.16	1.60	—	—	97.24
Zirkite (a)§	93.18	1.94	2.76	0.64	0.69	Trace	—	—	0.47	—	99.68
„ (b)§	81.75	15.49	1.06	0.85	0.50	Trace	—	—	0.63	—	100.28
„ (c)§	86.57	2.50	5.29	1.00	1.43	—	—	—	3.32	—	100.11

The purification of zirconia is not easy, particularly its separation from iron compounds, but it is desirable since the refractoriness increases with increasing purity. One method is to fuse the raw mineral with sodium carbonate and borax in an iron vessel, extract with water, filter and concentrate the solution until crystals separate.

Rossiter and Sanders|| have described a simple method for separating zirconia from iron and alumina. Up to the present, however, no sufficiently cheap process has been devised to allow of the use of pure zirconia as a refractory.

Zirconia is devoid of plasticity and is made up into articles¶ by adding one per cent. of starch and also some magnesia, thoria, or other vitrifiable earth, or alternatively by adding fireclay. For use at 2000° C. an addition of 1 per cent. of alumina is recommended in the first method, 1 per cent. of thoria for use at 2200°, and from 1 to 3 per cent. of yttria for use at 2400° C. These additions reduce the porosity of the product, whilst fireclay, in addition to increasing the density, causes a decrease in the refractoriness and limits the sphere of usefulness to temperatures below 1700° or 1800° C. According to H. E. Coley,** the problem of plasticity

* *Mining Magazine*, 1893.

† H. C. MEYER, *Chem. and Met. Eng.*, December, 1914.

‡ W. ROSENHAIN, *Trans. Faraday Soc.*, 1917, 12, 180.

§ H. C. MEYER, *Trans. Amer. Cer. Soc.*, 1918, 18, 264.

|| *J. Soc. Chem. Ind.*, 1921, 40, 70 T.

¶ O. RUFF and G. LAUSCHKE, *Sprechsaal*, 1916, 36, 70.

** *Chem. News*, 1920, 120, 7.

has been largely solved, and the shrinkage can be influenced by the use of grog in the form of previously fired and ground zirconia.

As already indicated, zirconia is very highly refractory. Ruff and Lauschke* give the fusion point of the oxide at a pressure of under 30 millimetres of mercury as $2563^{\circ} \pm 10^{\circ} \text{C.}$, and E. H. Rodd† states that even containing about 1.25 per cent. of silica and ferric oxide, zirconia does not melt below 2560°C. Washburn and Libman,‡ investigating the melting-points of mixtures of zirconia and silica, found that for use as a refractory up to 2550°C. , the presence of silica as an impurity in zirconia was not necessarily detrimental, since the addition of silica up to 33 per cent. eliminated its fluxing action. Such a refractory would have the properties of zirconium silicate, but would be nearly as resistant to high temperatures as pure zirconia. Refractories of considerable strength, it was suggested, could possibly be made from powdered zircon, bonded with a mixture of zirconium hydroxide and silica in molecular proportions and fired in an electric furnace. The estimated "true" melting-points of pure zirconia, natural zircon, and various zirconia-silica mixtures, determined by the same authors, are given in Table LXXIX.

TABLE LXXIX.—MELTING-POINTS OF ZIRCONIUM COMPOUNDS AND MIXTURES.

<i>Material.</i>	<i>Melting-Point.</i>	<i>Material.</i>	<i>Melting-Point.</i>
	(<i>Degrees C.</i>)		(<i>Degrees C.</i>)
Pure zirconia	2720	$\text{ZrO}_2, \text{SiO}_2$	2550
Natural zircon	2550	$2\text{ZrO}_2, 3\text{SiO}_2$	2420
$3\text{ZrO}_2, \text{SiO}_2$	2685	$\text{ZrO}_2, 2\text{SiO}_2$	2420
$2\text{ZrO}_2, \text{SiO}_2$	2650	$\text{ZrO}_2, 3\text{SiO}_2$	2420
$3\text{ZrO}_2, 2\text{SiO}_2$	2460		

Apart from refractoriness, the important property of zirconia is its low rate of thermal expansion ($\alpha = 0.0000084$).§ Crucibles made from it can be plunged red-hot into water without damage. Zirconia has also a very low conductivity for heat. Chemically, it is extremely inert, being highly resistant to acids, fused alkalis, fused quartz, or molten glass. In Rosenhain's|| opinion there is a great future for zirconia as a refractory in the glass industry, especially if it could be used, as he thinks possible, as a lining to pots made of less costly materials. Zirconia is, however, distinctly soluble in glass.

One undesirable property of zirconia is its tendency, at high temperatures in the presence of nitrogen or carbon, to form a nitride or carbide, particularly the carbide. This latter, whilst very hard and refractory, has not the other valuable properties of zirconia.

Crude zirconia ground to powder and mixed with bonding material forms very satisfactory bricks. Water-ground zirconia in an extremely

* *Loc. cit.*

† *J. Amer. Cer. Soc.*, 1920, **3**, 634.

‡ *J. Soc. Glass Tech.*, 1917, **1**, 130.

§ *J. Soc. Chem. Ind.*, 1918, **37**, 213 R.

|| E. H. Rodd, *loc. cit.*

fine state of division is perhaps the best bond, but lime, water-glass and zirconium nitrate have been used. Burnt at 1400° to 1500° C. the bricks shrink about 10 per cent. of the original volume, but the actual shrinkage varies with the size of the particles, being smallest where these are finest, and if the zirconia is previously burnt, there is also a reduction in shrinkage. Rosenhain* states that crude zirconia can be made up into bricks, bonded with a little china-clay or fireclay, which will resist fairly well a temperature of 1650° C. For the best results it is necessary to burn the material at a much higher temperature than that to which it is to be exposed, for otherwise it cracks, being a poor conductor of heat.

It is stated by H. E. Coley† that a satisfactory commercial process has been perfected for the manufacture of zirkite brick in America. At present, zirconia bricks of suitable shapes can be produced and fired, having a melting-point of not less than 2300° C., a low coefficient of expansion, a low heat conductivity, a resistance to slags better than other refractories, a capacity to resist very great pressures when cold and a greater pressure than other refractories when hot, and can be heated and cooled alternately and rapidly without deterioration. W. Rosenhain and E. A. Coad-Pryor‡ found that crude zirconia bricks lasted longer than magnesite bricks in their recuperative furnace, but they failed through the same cause—viz., spalling. The zirconia bricks, however, were eminently successful from the point of view of heat conservation, the gas consumption of the furnace for a standard working temperature of 1500° being decreased from 1,200 to 720 cubic feet per hour. A marked diminution in the temperature of the external walls of the furnace was noticed.

In addition to its use in brick form, zirconia is employed for the manufacture of drawn filaments for incandescent lamps, for the manufacture of small, highly refractory, laboratory utensils, and also as an addition to fused silica ware for the prevention of devitrification. An industrial test of zirconia cement,§ used as a wash for bungs in a malleable iron furnace, showed that the life of a bung was increased about 25 per cent. by the use of such a zirconia wash.

(214) **Asbestos**.—Asbestos, $\text{CaO}, 3\text{Mg}(\text{Fe})\text{O}, 4\text{SiO}_2$, is a neutral refractory used in the form of sheet or fibre. The fibre may be used as a packing to prevent conduction of heat or be made into bricks by admixture with fireclay (2 parts of fireclay to 1 part of asbestos). The bricks are light and porous, good for structures where resistance to high temperatures is necessary but where resistance to slags or abrasion is not needed.

Crucibles may be manufactured from asbestos by admixture with fireclay, magnesia or graphite, and water glass.

(215) **Basic Refractories**.—Lime, iron ores, dolomite and magnesia (magnesite) all basic refractories, have at present no extended use for glassworks refractories, but we would not say that they are incapable of utilisation.

* *Trans. Faraday Soc.*, 1917, 12, 180.

† *Engineering*, 1919, 107, 702.

‡ *M. SHEPPARD, J. Amer. Cer. Soc.*, 1921, 4, 662

† *Loc. cit.*

Alumina.—Pure alumina is one of the most refractory materials known, but is entirely devoid of plasticity. The common form of alumina, used in the manufacture of refractories, is bauxite, a hydrated alumina, $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, usually containing iron oxide. Searle* gives the analytical composition of three samples of bauxite, and these are shown in Table LXXX.

TABLE LXXX.—PERCENTAGE COMPOSITIONS OF BAUXITES.

<i>District Found.</i>	SiO_2 .	Al_2O_3 .	Fe_2O_3 .	CaO .	MgO .	<i>Loss on Ignition, Etc.</i>
Arles, France ..	9.0	70.4	5.1	0.6	0.7	14.2
Herault, France ..	14.7	65.1	5.4	1.3	0.9	12.6
Belfast	14.5	41.3	28.7	1.7	0.2	13.6

Some samples of bauxite contain up to 90 per cent. of alumina. The best types for refractory purposes are those which contain as little silica, iron oxide, and titanium oxide as possible; more than 10 per cent. of iron oxide (Fe_2O_3) is very objectionable.

For the making of bricks the bauxite is washed and the purer material is selected. This is burnt, crushed, and mixed with one-third to one-sixth of its bulk of plastic fireclay; water is added and the mass brought to condition for moulding. Bauxite bricks are among the best for resistance towards abrasion. Although chemically very inert and mechanically strong, alumina shrinks considerably, and this is a great disadvantage. The shrinkage difficulty might be overcome by burning the bricks at a very high temperature.

Bauxite may also be added to fireclay to increase its refractoriness, but must be added in a finely divided state and worked in well, or the mechanical strength of the brick is reduced.

Another form of alumina used as a refractory material is alundum or artificial emery, Al_2O_3 . Alundum is made by calcining bauxite in the electric arc. The product fuses at 2300° , and is used for analytical apparatus, crucibles, muffles, tubes, etc. Bricks have also been made from it, but the cost of these is at present prohibitive. Makers of refractory alundum articles, bonded with a small percentage of fireclay, state that their melting-point is 2050°C ., coefficient of expansion 0.000071, maximum crushing strength 15,410 pounds per square inch, and tensile strength 1,700 pounds per square inch.

(216) **Acid Refractories.**—The acid refractories are those which consist of silica alone or have a high proportion of silica. Silica may occur in a hydrated form, but as a refractory material we are mainly concerned with silica in its crystalline and, in a lesser degree, its amorphous forms.

(217) **The Allotropic Forms of Silica.**—According to Fenner,† silica exists in at least seven crystalline forms, and before considering in detail

* *Refractory Materials*, C. Griffin and Co., Ltd., 1917.

† *Amer. J. Sci.*, 1913, 36, 331.

the various refractories containing silica it is necessary to learn something of these various forms.

Quartz is the type of silica which is most common. It varies considerably in form and colour, due to the inclusion of impurities, but the transparent, colourless crystals known as "*rock crystal*" are practically pure silica. *Chalcedony*, which has frequently been regarded as a distinct variety of silica, is not, according to Wietzel,* a distinct form, but is microcrystalline quartz. This was neglected by Fenner and not included in his seven forms. The three most important modifications of silica are *quartz*, *tridymite*, and *cristobalite*. Each of these exists in two different forms, known as the α and β phases, and each can be converted into either of the other forms by appropriate heat treatment. At ordinary temperatures the α phases exist, and these pass into β phases as the temperature rises. The α to β transformations are reversible and rapid, and may possibly consist merely of a slight rearrangement of the molecules within the crystal structure. The transformation from one crystalline form to another is generally very slow, especially near the inversion temperature. The inversion temperatures, according to Fenner, are—

α quartz	—>	β quartz	at 575° C.
β quartz	—>	α quartz	„ 570° C.
quartz	⇌	tridymite	„ 870° ± 10° C.
α tridymite	⇌	β_1 tridymite	„ 117° C.
β_1 tridymite	⇌	β_2 tridymite	„ 163° C.
tridymite	⇌	cristobalite	„ 1470° ± 10° C.
α cristobalite	—>	β cristobalite	„ 274.6° to 219.7° C.
β cristobalite	—>	α cristobalite	„ 240.5° „ 198.1° C.

The reversions on cooling are not sharp, and the temperature at which the *cristobalite* transformations occur depend upon previous heat treatment.

Cristobalite may develop as a metastable intermediate phase below 1470° C., and, in fact, when *quartz* is heated without a flux to high temperatures (not above 1470° C.) it is changed to *cristobalite* and not *tridymite*. In the presence of a flux or catalyst such as the lime used in silica brick manufacture, the change from *quartz* to *cristobalite* (not *tridymite*) occurs at as low a temperature as 1250°, though at this temperature the change is extremely slow.

According to Rees† the stability relations of the various forms of silica, particularly of *tridymite* and *cristobalite*, are still in doubt. Certainly work done during recent years by Le Chatelier and by Scott‡ appears to conflict with Fenner's conclusions. On the other hand, recent work by Ferguson and Merwin§ had indicated that the melting-point of *tridymite* (1670° ± 10° C.) was considerably lower than that of *cristobalite* (1710° ± 10° C.). It followed necessarily from this observation that *cristobalite* was the high-temperature form.

Endell and Riekel|| had found previously that, in their experiments with silica bricks, *quartz* apparently inverted to *cristobalite* and then to

* Zeitsch. anorg. Chem., 1921, 116, 71.

† Trans. Eng. Cer. Soc., 1918, 17, 459.

‡ Zeitsch. anorg. Chem., 1913, 79, 239.

§ J. Soc. Glass Tech., 1918, 2, 253.

|| Amer. J. Sci., 1918, 48, 417.

tridymite, whilst Le Chatelier* states definitely that *tridymite* is the only crystalline form of silica which is perfectly stable at high temperatures. On the other hand, Klein† burned and reburned bricks at 1540° C., and *cristobalite* was the only inversion product noted. Insley and Klein‡ declare that "the presence of *tridymite* in bricks which have had maximum burning temperatures above the *tridymite-cristobalite* inversion point seems difficult of explanation. It is possible in cases where the brick did reach these high temperatures that during the greater portion of the heating period its temperature was well below the inversion point. It is probable, too, that while the temperature recorded in the kiln was above 1470° C. the temperature below the surface of the brick was not nearly so high." They conclude that their investigations have "verified the prediction of Fenner that, with a comparatively small amount of flux, quartz inverts to *cristobalite*, then to *tridymite* at temperatures where *cristobalite* is the unstable and *tridymite* the stable modification. In the case of every brick examined, *cristobalite* was the first inversion product to form, whether the burning conditions had been such as to promote much or little inversion. Moreover, the final inversion product, reached after many reburnings to the temperature range where it was the stable modification, resulted invariably in the formation of *tridymite*."

The practical importance of these silica transformations lies in the accompanying volume changes which will be dealt with in the discussion of the behaviour of silica bricks on heating.

As examples of highly siliceous materials used as refractories we may instance sands, quartzites, Dinas rocks, ganister, firestones, kieselguhr, and fireclays.

Sands.—Sands (which have already been dealt with in Chapter VII.), though they consist chiefly of silica, have their refractoriness influenced by the presence of impurities. Ferrous oxide brings about a considerable lowering of the fusion-point. The presence of alumina also lowers the fusion-point, as shown in Fig. 88,§ the material being least refractory when it contains 10 per cent. of alumina. Lime also has a considerable effect in reducing the refractory character of sands, as shown in the same diagram.

(218) **Silica Rocks.**—Silica rocks are chiefly composed of quartz or quartzite, and may contain up to 99.6 per cent. of silica. When pure, quartz grains resemble small irregular fragments of glass, but they may also be cloudy and even opaque from impurities. Being devoid of plasticity, quartz acts as a diluent in clay, reduces its shrinkage on drying and firing, making it "short" or "lean."

A **quartzite** is a mosaic of grains of silica, cemented by iron oxide, lime, or by silica deposited from solution. The quartz may be derived, as sand, from feldspathic rocks by decomposition, and the quartzite produced by the action of pressure on the sand deposited, as a result of which the grains lose their individuality and form a mosaic. Many forms of such rock are found in this country.

* *Rev. Mét.*, 1917, 14, 74.

† See SEAVER, *Trans. Amer. Inst. Min. Eng.*, 1916, 53, 125.

‡ Bureau of Standards *Technologic Paper* No. 124, July 11, 1919.

§ HECHT, SEGER, AND SIMONIS, *Sprechsaal Kaltr.*, 1922, 14, 198.

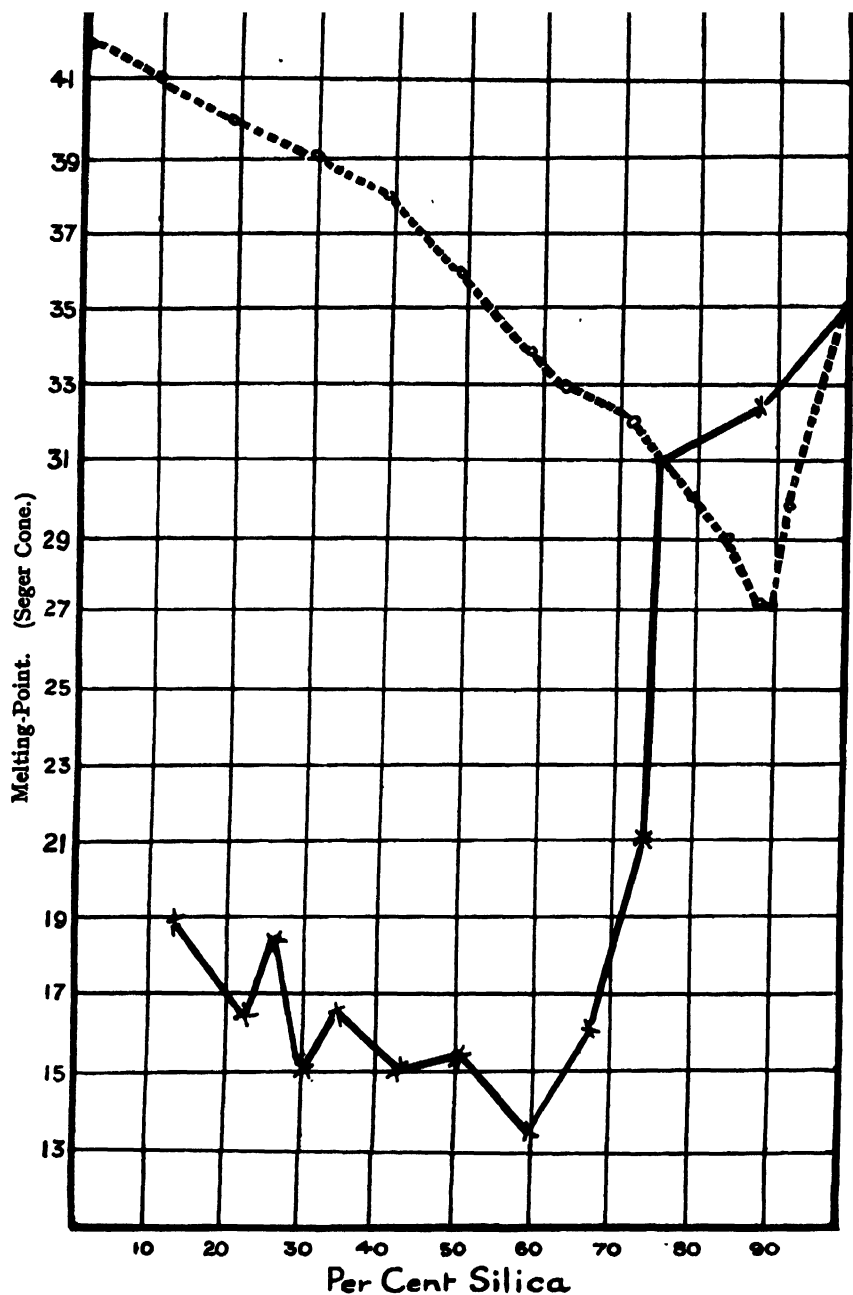


FIG. 88.—CURVES SHOWING THE EFFECT OF ALUMINA (DOTTED LINE) AND LIME ON THE MELTING-POINT OF SILICA.

The chemical composition and physical characteristics of quartzites vary considerably. Quartzites derived from geological formations earlier than the coal measures are seldom of much value for manufacturing purposes. For successful use as raw material in silica brick-making it is found that the quartzite must contain a considerable amount of tridymite, which acts as a binding material. As the conversion of tridymite into quartz is very slow, tridymitic materials may be obtained naturally in large quantities in some localities. Searle* states that for the best quality silica bricks the quartzite used should have the following properties:

- (1) It should contain a basal cement as shown by examination under the microscope.†
- (2) Impurities must be finely divided.
- (3) Maximum expansion and minimum specific gravity should be reached during the first burning to 1450° C.
- (4) It should contain 96 to 98 per cent. of silica.
- (5) The softening point must not be below cone 33 (1730° C.).

One of the most famous quartzites is Dinas rock from the Vale of Neath, Glamorganshire. This material occurs both as rock and sand. Typical analyses are given in Table LXXXI.

TABLE LXXXI.—ANALYSES OF DINAS ROCK.

Sample.	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	Alkalis.	Water, etc.
No. 1	98·31	0·72	0·18	0·22	0·14	0·35
No. 2	96·73	1·39	0·48	0·19	0·20	0·50

Ganister is an argillaceous sandstone containing up to 10 per cent. of clay. Its composition varies, as shown in Table LXXXII.

TABLE LXXXII.—ANALYSES OF GANISTER.

Sample.	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	Alkalis.	Water, etc.
Hard ganister† ..	97·9	0·6	0·3	0·6	0·2	—	0·4
Soft ganister† ..	88·4	6·4	1·7	0·7	0·4	—	2·4
Bonnymuir† ..	97·8	0·2	0·2	0·4	0·4	0·2	0·7
Lowood, Sheffield	89·04	5·44	2·65	0·31	0·17	—	2·3

The amount of clay varies considerably. Assuming the formula of clay to be Al₂O₃·2SiO₂·2H₂O, the above Lowood ganister works out as follows:

Silica (in excess of that in the clay)	81·28 per cent.
Clay	15·30 ..
Impurities	3·13 ..
Moisture and organic matter	0·20 ..

* *Loc cit.*

† McDOWELL has stated that the American quartzites which make the best bricks are free from cement, and consist wholly of interlocking crystals. Such a statement does not apply to British bricks.

‡ SEARLE, *loc. cit.*

The following specification is given by Searle* for ganister used as a refractory material:

Silica	87	to 96	per cent.
Alumina	4	"	5
Iron oxide (Fe_2O_3)	0	"	1.5
Lime and magnesia	0.25	"	0.75
Alkalis	0	"	1.0

For making bricks the ganister need only be crushed and mixed with water, since the clay-like bond affords the required plasticity. When larger blocks are to be made, a little lime may be added and a proportion of fireclay.

Firestone, as used in glass tank furnaces for sides and bottom, contains a high percentage of silica, and typical analyses are given in Table LXXXIII.

TABLE LXXXIII.—ANALYSES OF FIRESTONES.†

Sample.	SiO_2 .	Al_2O_3 .	Fe_2O_3 .	SiO_2 .	CaO .	MgO .	K_2O .	Na_2O .	Loss.
Mexborough ..	80.96	10.96	1.32	0.80	0.30	0.50	2.48	1.10	2.14
Wickersley ..	83.13	8.83	2.23	0.70	0.31	0.16	2.06	0.87	2.03
Durham ..	89.50	6.23	0.77	0.65	0.27	0.31	0.84	0.44	1.58

Kieselguhr, or diatomaceous earth, consists of the skeletons of diatoms, extremely minute plants having an external silica coating. It is found in Germany, Barbados, Ireland, and other places. It is useful as a non-conducting, packing medium, but may also be made into light bricks with clay. W. C. Phalen‡ gives the analyses of kieselguhr shown in Table LXXXIV.

TABLE LXXXIV.—ANALYSES OF KIESELGUHR.

Sample.	SiO_2 .	Al_2O_3 .	Fe_2O_3 .	CaO .	MgO .	K_2O .	Na_2O .	H_2O .	H_2O .
No. 1 ..	81.53	3.43	3.34	2.61	—	1.16	1.43	6.04 §	—
No. 2 ..	75.68	9.88	2.92	0.29	0.69	0.02	0.08	—	9.21
No. 3 ..	73.50	11.71	2.35	0.32	0.83	1.88	—	9.54	—
No. 4 ..	86.89	2.32	1.28	0.43	Trace	3.58	—	4.89	—

Fused quartz, an amorphous form of silica, is a very useful refractory for some purposes. It is obtained by melting sand in an electrical resistance furnace at temperatures between 1800°C . and 2000°C . Cylinders or tubes, rods, lamp-glasses, crucibles, and other moulded ware are made from fused silica.

* *Loc. cit.*

† J. H. DAVIDSON, *J. Soc. Glass Tech.*, 1917, 1, 127.

‡ *British Clayworker*, 1920-21, 29, 148.

§ Figures include organic matter.

|| Figures include nitrogenous matter.

CHAPTER XXI

SILICA BRICKS

IN general, the term silica brick includes Dinas bricks, ganister bricks, and clay-silica bricks. In Dinas bricks, the particles of siliceous rock are bonded with lime. In ganister there is a natural mixture of silica with a certain amount of clay, frequently sufficient to make a bond. When necessary, a little more clay may be added. Clay-silica bricks usually contain equal parts of silica and fireclay, but seldom more than two parts of silica to one of clay.

(219) **Raw Materials.**—M. Phillipon* considers that by suitable treatment satisfactory bricks may be made from any variety of quartz rock. There is very little doubt, however, that the quartz is more readily inverted in the case of ganister, and a good brick can be made with a smaller expenditure of fuel in this case than when other forms of quartz are used. Sand is usually unsuitable for the manufacture of silica bricks because it gives them too great a porosity and too low a strength. According to Dauphin,† however, if a portion of the sand is ground so fine that it passes wholly through a 50-mesh sieve and half of it passes through a 200-mesh sieve, it may be used quite satisfactorily provided the sand is sufficiently pure.

The bond used is usually lime slurry. Lime reduces the refractoriness of the silica and should never exceed 2 per cent. of the brick. It has been found‡ that bricks containing 3 per cent. of lime and mixed by hand are not as strong as those containing only 1 per cent. which have been tempered in an edge runner mill. Insley and Klein§ state that although the addition of lime hastens the inversion of silica and thus increases the strength of the brick, the lime itself, and the compounds which it forms, seem to play but a small part in the cementing of the finished brick. Most of the bonding action of the brick seems to come from the interlocking of the cristobalite and tridymite crystals. The glass, which sometimes appears to form a matrix for the tridymite crystals, may also aid in the bonding of the bricks.

Le Chatelier and Bogitch|| have shown that the use of a considerable proportion of impalpable silica powder (such as slimes from the acid purification of gold ore) having grains about 0.01 millimetre in diameter, accelerates the recrystallisation of the quartz as tridymite, and very

* *Compt. rend.*, 1917, **165**, 1,002.

† DAUPHIN, *ibid.*

|| *Compt. rend.*, 1917, **165**, 742.

† *Bull. Soc. de l'Ind. Min.*, 1918, **13**, 137.

§ *Loc. cit.*

considerably increases the mechanical strength of the brick at high temperatures. They recommend a mixture of 75 parts of raw quartzite of particles up to 4 millimetres diameter, 25 parts of impalpable silica, and 2 parts of lime. When dried, the bricks so made have a crushing strength of 15 kilograms per square centimetre; when fired five days to cone 19, of 165 kilograms per square centimetre; and after one hour heating at 1600° C. of 30 kilograms per square centimetre.

The presence of alumina in the raw silica materials is undesirable and reduces the refractoriness. When it occurs as clay or silicates it is probably the most active of all the fluxing impurities in silica brick. It should not exceed 1.5 per cent. of the brick. Iron oxide may not be so undesirable since magnetic oxide of iron, which is the stable form at high temperatures, neither combines with silica nor forms a solid solution at high temperatures. Iron oxide may have greater effect in reducing the refractoriness if excess of lime is also used. At least 5 per cent. of ferric oxide may be added to a silica brick mixture without materially lowering its refractoriness.

(220) **Methods of Manufacture.**—Hand moulding is usually done in steel-faced moulds open top and bottom. The raw material is tamped down with heavy beaters, an operation which requires to be performed very carefully and evenly. Objections have frequently been made to bricks made by machine. The material must be worked drier in the machine than by hand, and a great pressure is required. The greater the pressure used in shaping the bricks, the stronger are the bricks and the smaller is the loss in manufacture. There is no doubt that machine-made bricks of best quality are superior in shape, general appearance, and in resistance to corrosion by slags to the hand-made variety.

The bricks may be air-dried rapidly, then set checkerwise in a kiln, heated slowly at first, and then gradually brought to a temperature of about 1500° C., this temperature being maintained for a considerable number of hours.

(221) **The Properties of Silica Bricks.**—As was indicated in an earlier section, the most important effect of the inversions of silica, as regards the practical application of silica bricks, lies in the volume changes which accompany them. According to Insley and Klein,* the complete transformation of *quartz* to *cristobalite* gives a volume increase of 13.6 per cent., and *quartz* to *tridymite* of 16.8 per cent. McDowell† finds that the permanent expansion of commercial silica bricks amounts to 10 or 11 per cent., by volume.

In an admirable short paper on silica refractories for glassworks' use, Rees‡ divides the total expansion of a silica brick in the furnace into three phases: first, the ordinary thermal or temporary expansion, which is reversible and is due to both the usual thermal expansion and to the volume change from the reversible α - β *quartz* (and α - β *cristobalite*) inversions; secondly, the permanent expansion due to inversion of the original *quartz* to *tridymite* or *cristobalite*; and thirdly, the increase in volume, which can be ascribed to the fact that when the *quartz* is converted to *tridymite* or *cristobalite*, the newly formed crystals are not

* Loc. cit.

† Bull. 119, Amer. Inst. Min. Eng., November, 1916.

‡ J. Soc. Glass Tech., 1918, 2, 253.

so oriented as to occupy the minimum volume, and consequently occupy more space than would be inferred from the reduction in specific gravity.

The first volume change cannot be avoided. As regards the permanent expansion, if the silica is all converted to *tridymite* during the burning, the brick will have reached the limit of permanent expansion. Not only this, but it will have improved crushing strength, cross-breaking strength and resistance to spalling. The difficulty arises, however, that the length of time required and the fuel expended in producing an all-*tridymite* brick would make its price prohibitive, but the nearer the brick approaches this "ideal" state the better will it behave in practice. Since expansion of silica bricks in the furnace structure is bound to occur on heating and contraction on cooling, constant attention to furnace tie-rods is necessary to prevent serious damage. Tension on these must be relieved during heating and increased during cooling.

The volume changes indicated are accompanied by changes in specific gravity. These changes are slow, as was shown by Endell and Rieke,* whose results are quoted in Table LXXXV.

TABLE LXXXV.—CHANGES IN SPECIFIC GRAVITY OF SILICA ON HEATING.

Material.	Specific Gravity.						
	Raw.	After Heating the Number of Times Specified.					
		1	2	4	6	8	10
Hohenbocka quartz sand	2.651	2.591	2.502	2.450	2.428	2.369	2.338
St. Gothard quartz crystal in pieces	2.650	—	—	—	2.64	—	2.63
St. Gothard quartz crystal powdered	2.650	2.568	2.553	2.519	—	—	—
Flint	2.632	2.231	2.241	2.239	2.255	2.231	—
Chalcedony	2.607	2.16	2.17	2.17	2.19	—	—
Fused quartz	2.21	2.327	2.328	—	—	—	—

The rate of change depended on the type of quartz and on the size of the particles. Figures given by different authorities for the specific gravity of the various forms of silica are shown in Table LXXXVI.

Le Chatelier† states that at 1000° C., *tridymite*, *cristobalite*, and glassy silica have all approximately the same specific gravity—viz., 2.20.

The apparent density of silica bricks varies considerably. The porosity ranges from about 4 to 20 per cent., whilst the specific heat is about 0.26 (see p. 303). The thermal conductivity of silica brick is generally lower than that of fireclay brick. It increases with the firing temperature, and silica bricks burned at 1300° have a conductivity 50 per cent. greater than those burned at 1050° C.‡

* *Silicat-Zeitschrift*, 1913, 2.

† *Rev. Mët.*, 1917, 14, 74.

‡ E. GRIFFITHS, *Trans. Faraday Soc.*, 1917, 12, 193.

TABLE LXXXVI.—THE SPECIFIC GRAVITIES OF VARIOUS FORMS OF SILICA.

<i>Form of Silica.</i>	<i>Specific Gravity.</i>	<i>Authority.</i>
α -quartz	2.65	Le Chatelier
β -quartz	2.63	—
α -cristobalite	2.33	Endell, Le Chatelier
Artificial cristobalite	2.33	Fenner
Natural cristobalite	2.34	Mallard
β -cristobalite	2.21	—
α -tridymite	2.32	Endell
α -tridymite	2.27	Le Chatelier
Artificial tridymite	2.27	Fenner.
Natural tridymite	2.28	Mallard
β -tridymite	2.32	—
Quartz glass	2.21	Dana, Endell
"	2.19	Schwartz
Fused silica	2.22	Le Chatelier

Silica bricks stand up under load better than fireclay brick. Fine grained silica bricks do not stand under load so well as coarser-grained samples. The resistance of silica bricks to abrasion and slag action is low, and they are consequently used only for the upper parts and crowns of furnaces. Mellor and Emery* state that in silica bricks the depth of penetration by the flue dust in furnaces is generally less the finer their grain. The bond of a silica brick offers the feeblest resistance to the attack of a corrosive slag. Under oxidising conditions, iron oxide does not corrode silica bricks to any noteworthy extent, but under reducing conditions ferrous silicate may act as a corrosive flux. When the ferruginous dust forms a surface glaze the brick is protected from further attack, or the subsequent rate of attack is considerably diminished. "Furnace drops," which are formed on the silica crowns of glass tank furnaces by the action of alkaline dust and vapours, are readily soluble in the glass and do not tend to form stones. In the case of fireclay bricks, droppings form "stones" much more readily.

(222) **Specifications.**—Silica bricks must meet the following requirements; they must—

- (1) Be infusible at the highest temperatures of the furnace.
- (2) Be mechanically strong after being burned, and
- (3) Show small change in volume on heating.

Dauphin† suggests that typical silica bricks of the best quality and medium quality respectively should have the following properties:

	<i>Best.</i>	<i>Medium.</i>
Refractoriness (T)	1750° C.	1730° C.
Refractoriness after adding 6 per cent. of Fe_2O_3 (t)	1735° C.	1710° C.
True specific gravity	2.35	2.47
Porosity	18 per cent.	20 per cent.

The durability is a function of T and t . No brick should have T less than 1730° C. and t less than 1716° C. The porosity should not be usually less than 18 per cent., whilst 2.47 for the specific gravity should be regarded as the strict maximum.

The "Provisional Specifications for Glass Refractories," issued by the Society of Glass Technology, include the following specification* for silica bricks:

"At the desire of the purchaser, the following data shall be supplied for his personal information only, with average samples true to bulk:

"(a) Analysis.

"(b) Refractoriness.

"(c) Linear expansion after being heated to cone 12."

SPECIFICATION.

1. *Chemical Composition*.—The bricks shall contain not less than 94 per cent. of silica and not more than 2 per cent. of lime.

2. *Refractoriness*.—Test-pieces shall not be more fusible than cone 32 (about 1710° C.). The test shall be carried out in an oxidising atmosphere, the temperature of the furnace being increased at the rate of about 50° C. per 5 minutes.

3. *After-Expansion*.—A test-piece, after being heated to temperature equivalent to cone 12 for two hours, shall not show, on cooling, more than 0.75 per cent. linear expansion.

4. *Texture*.—The bricks shall be uniformly burnt, and shall have a regular texture, with no holes or flaws.

5. *Variations from Measurements*.—All surfaces shall be reasonably true, and there shall not be greater variation than ± 2 per cent. from any specified dimension.

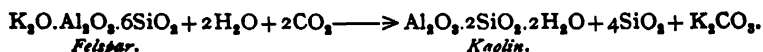
(223) **Silica Cement**.—Silica cement consists of a high quality silica rock together with not more than 5 or 6 per cent. of good fireclay. The provisional specifications mentioned previously include the following: "Silica cement shall in all cases be finely ground and suitable for binding together the bricks for which it is supplied. It shall contain not less than 92 per cent. of silica, and shall be capable of withstanding the same test for refractoriness as the brick."

* *J. Soc. Glass Tech.*, 1919, 3, 6.

CHAPTER XXII

FIRECLAYS

(224) **Origin.**—The great advantage of fireclays is that, whilst they are refractory, they can be moulded readily into any shape. They are always of secondary origin, resulting primarily from the decomposition of rocks, mainly felspathic (see Chapter VIII.), by weathering—*i.e.*, the action chiefly of water and carbon dioxide. If the rock be pure felspar, the production of a pure kaolin may probably be represented thus—



Where the clay is obtained, however, from granite, silica and mica may remain with such clay, as these are present in the rock. Hence there will be a number of impurities present.

Clay in its purest form, therefore, shows the following results on analysis:

Alumina (Al_2O_3)	39.7 per cent.
Silica (SiO_2)	46.4 "
Water (H_2O)	13.9 "

With the exception of pure china clay, the composition of fireclay is distinctly different from the above, and it is not a homogeneous chemical compound, but is usually taken to be a mixture of—

- (a) True clay, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$;
- (b) Quartz, SiO_2 (as sand, etc.); and
- (c) Felspars, remaining undecomposed.

According to Le Chatelier,* the statement that clay is a mixture of the true clay, quartz, and felspar is not correct, as felspar is practically never present in clays. All the potash in the clay is there in the form of mica, $6\text{SiO}_2 \cdot 3\text{Al}_2\text{O}_3 \cdot \text{K}_2\text{O} \cdot 2\text{H}_2\text{O}$. This is confirmed by the fact that nearly all the potash is soluble in sulphuric acid, which would not be the case with felspar. When examined under the microscope, feebly plastic clays have well developed crystalline forms, the medium clays contain fragmentary crystals, whilst the plastic clays consist of very fine irregular particles, showing the gradual breaking down of the crystalline quartz and felspars to the non-crystalline true clay.

(225) **The Occurrence of Clays.**—Clays belong to all geological periods, some being soft and plastic, others having lost the hygroscopic water

* *Trans. Faraday Soc.*, 1917, 12, 135.

and become dry. A further stage is reached if the clay has been subjected to great pressure, for it then loses also combined water and is non-plastic. It has been shown* that the loss of the so-called combined water at ordinary temperatures does not result in any drastic change in the structure of the clay molecule, for the water can be restored in a moist atmosphere. This is quite different from what occurs when water is expelled at higher temperatures.

Many of the fireclays are found associated with the coal measures, and these carboniferous clays are usually dark in colour, due to organic matter, but they may burn white. The sedimentary clay beds usually assume horizontal parallel structure, caused by the pressure of layers which are of different composition; that is, at different levels we have clay layers which may vary distinctly in composition and properties, whilst any one seam may also be composite.

Thus, in the Stourbridge Old Mine Seam there are found in the 4-foot depth,

- (1) At the top, mild clay, rich in alumina.
- (2) At the middle, a medium clay (pot clay).
- (3) At the bottom, strong or siliceous clay.

(226) **Classification of Clays.**—Clays may be classified in different ways, according to their origin, uses, or composition and properties. Orton's classification is as follows:

A. High Grade Clays (50 per cent. or more of "true clay," with silica).

- | | |
|--------------------|------------------------|
| 1. Kaolin. | 4. Fireclay (strong). |
| 2. China-clay. | 5. Fireclay (plastic). |
| 3. Porcelain clay. | 6. Potter's clay. |

B. Low Grade Clays (10 to 70 per cent. "true clay," with a variable flux content).

- | | |
|------------------------|-----------------------|
| 1. Argillaceous shale. | 4. Tile clays. |
| 2. Ferruginous shale. | 5. Brick clays. |
| 3. Siliceous clays. | 6. Calcareous shales. |

Riest† classifies clays into three sections: (a) residual clays, (b) coluvial clays, and (c) transported clays. The residual clays include kaolins or china clays, whilst the transported clays include most of the fireclays and refractory shales used in the glass industry.

A classification into fat, lean, plastic, slate, bituminous, marl and mud divisions may be made, but there is no really satisfactory general method of classifying clays.

(227) **The Chemical Composition of Clays.**—In the examination or testing of clays, one of the tests almost invariably carried out is the chemical analysis. It is assumed that the various components of the clay exist as oxides, but, as has already been indicated, this is by no means the case. Usually the chemical compositions of fireclays and

* MELLOR, SINCLAIR AND DEVEREUX, *Trans. Eng. Cer. Soc.*, 1921-22, **21**, 104.

† "CLAYS: THEIR OCCURRENCE, PROPERTIES, AND USES." *Chapman and Hall, Ltd.*, 1914.

refractory shales used in the glass industry are expressed under nine headings as follows:



and the "loss on ignition." The loss on ignition may include combined water, organic matter, carbon dioxide, and sulphur trioxide, but not uncombined moisture, which should always be removed by drying the clay sample thoroughly in an air-oven at 110°C . before commencing the analysis. The carbon dioxide and sulphur trioxide are usually quite small in proportion.

The ultimate analysis of clays is of very doubtful value. It is always a lengthy and tedious process, and, *per se*, only occasionally affords much reliable information as to the possible value of the clay in commercial practice. One extremely important use of the ultimate analysis of clays for the glass industry is to indicate the nature and amount of the impurities present. As is well known, one of the most deleterious impurities in clays required for glassworks' furnace or pot construction is iron oxide. If, therefore, it is found that the clay contains an abnormal amount of iron oxide it may be rejected without undergoing any further tests, similarly with other fluxing impurities, such as lime, magnesia, potash, soda, and, in a much less degree, titanium oxide. A very high silica content may be indicative of a sandy clay, but otherwise it does not afford much information. Any other inferences as to the practical value of the clay which may be drawn from the chemical analysis must be carefully examined. The physical properties, such as the plasticity, drying and firing shrinkage, density and mechanical strength, can rarely, if ever, be even remotely determined from the ultimate analysis.

Quite a number of attempts have been made to establish a relationship between the refractoriness of a clay and its chemical composition. Bischof's formula was—

$$Q = \frac{a^2}{bc},$$

where Q = the so-called refractory coefficient of the clay,

a = the oxygen content of the alumina,
 b = " " " " silica,
 c = " " " " fluxes.

For refractory materials Q varied between 2 and 14, first-class fire-brick having a value between 6 and 14. The method is open to many objections and exceptions are frequently noticed.

Seger modified the formula to

$$Q = \frac{a(a+b)}{b}.$$

where a = ratio of alumina to fluxes taken as unity,
 and b = " silica " " " "

Seger's formula is better than that of Bischof in some respects, but both neglect the influence of homogeneity, porosity, fineness of grain and

atmospheric (reducing or oxidising) conditions upon the softening or fusing temperatures of the clay. The best method of determining the refractoriness of a clay is by direct experiment.

Early in 1919, the Refractories Research Committee of the Society of Glass Technology was able, after several months of discussion, to complete a provisional specification* for glassworks' refractory materials. Included, amongst other things, was an attempt to classify fireclays suitable for glass refractories into three grades, according to their chemical composition. Researches† carried out subsequently under the auspices of the Committee brought out the fact that, if the clays actually examined were brought up for judgment according to the standards set out, the bulk of the British clays studied were condemned unless they could be purified. The specification is accordingly undergoing review.

The researches mentioned were conducted upon samples from twenty-seven sources. In Table LXXXVII. are shown the extreme figures for each constituent determined, and the wide variation in composition of British clays will be at once apparent. Attempts made to link up the chemical compositions with the values of the properties of the clays measured were very disappointing.

TABLE LXXXVII.—MAXIMUM AND MINIMUM OXIDE CONTENTS OF BRITISH CLAYS.

<i>Constituent.</i>	<i>Highest Figure.‡</i>	<i>Lowest Figure.‡</i>
	<i>Per Cent.</i>	<i>Per Cent.</i>
Silica (SiO_2)	75.60	42.36
Alumina (Al_2O_3)	52.48	19.02
Iron oxide (Fe_2O_3)	5.62	1.16
Titanium oxide (TiO_2)	4.33	1.03
Lime (CaO)	0.53	Nil
Magnesia (MgO)	0.99	Trace
Potash (K_2O)	2.83	0.34
Soda (Na_2O)	1.07	Trace

The losses on ignition varied between 14.95 and 6.24 per cent. of the raw clay.

Whilst it is at present almost impossible to forecast the softening or fusion-point of a clay by a consideration of its composition, it is quite easy to make mixtures of materials such as oxides which have definite and reproducible fusion-points. This fact is made use of in the manufacture of Seger cones. These were first introduced by Seger, and consisted of a series of mixtures of clays with fluxes, so arranged that they represented a series of squatting-points with intervals of 20° C. or 30° C. The original series has been extended by Cramer, Hecht, and others, and now numbers 64 cones (they are tetrahedrons really) with fusion-points varying from 590° C. to the fusion-point of alumina. In

* *J. Soc. Glass Tech.*, 1918, 2, 272.

† FIRTH, HODKIN, and TURNER, *J. Soc. Glass Tech.*, 1920, 4, 162.

‡ Calculated values after ignition.

Table LXXXVIII. a number of these cone compositions are specified, together with their squatting temperatures.

For use they are placed in the furnace, kiln, or other place in such a position that they can be seen but be out of actual contact with the flames. Several cones are used, some indicating temperatures below and some above that required. When the temperature reaches that corresponding to the most easily fusible cone, the top of the cone bends over. By careful adjustment the temperature can then be so arranged that the cone corresponding nearest to the temperature required bends over until the top is level with the base. The rate of heating must be carefully regulated if the cones are to register their specified temperature, and the temperature should be raised at an average rate of about 5°C . per minute.

TABLE LXXXVIII.—COMPOSITIONS AND SQUATTING TEMPERATURES OF SEGER CONES.

Number of Cone.	Composition.	Squatting-Point.
		Degrees C.
022 ..	$2\text{SiO}_2, \text{B}_2\text{O}_3, 0.5\text{Na}_2\text{O}, 0.5\text{PbO}$	590
015 ..	$3.2\text{SiO}_2, \text{B}_2\text{O}_3, 0.5\text{Na}_2\text{O}, 0.5\text{PbO}, 0.6\text{Al}_2\text{O}_3$	800
07 ..	$3.65\text{SiO}_2, 0.35\text{B}_2\text{O}_3, 0.3\text{K}_2\text{O}, 0.7\text{CaO}, 0.2\text{Fe}_2\text{O}_3, 0.3\text{Al}_2\text{O}_3$	1010
1 ..	$4.0\text{SiO}_2, 0.3\text{K}_2\text{O}, 0.7\text{CaO}, 0.2\text{Fe}_2\text{O}_3, 0.3\text{Al}_2\text{O}_3$	1150
11 ..	$12\text{SiO}_2, 0.3\text{K}_2\text{O}, 0.7\text{CaO}, 1.2\text{Al}_2\text{O}_3$	1350
21 ..	$44\text{SiO}_2, 0.3\text{K}_2\text{O}, 0.7\text{CaO}, 4.4\text{Al}_2\text{O}_3$	1550
27 ..	$200\text{SiO}_2, 0.3\text{K}_2\text{O}, 0.7\text{CaO}, 20\text{Al}_2\text{O}_3$	1670
28 ..	$10\text{SiO}_2, \text{Al}_2\text{O}_3$	1690
36 ..	$1.5\text{SiO}_2, \text{Al}_2\text{O}_3$	1850
42 ..	Al_2O_3	(about) 2000

(228) **The Mechanical Analysis of Clays.**—The sizes of the particles of a clay have a most distinct influence on its physical properties. A test of the fineness of a clay may be made roughly by sifting, but if it is desired to measure more accurately the size of grains in the clay then a more elaborate method of separation is necessary. The method used is that commonly known as eleutriation. The clay is stirred with water, or, better still, is thoroughly shaken with water on a shaking machine. This thoroughly disintegrates the clay, after which it is subjected to the action of a current of water. By varying the speed of flow, particles of different sizes are separated out. By varying from a high to a low rate of flow there may be separated out in turn, for example, sand, fine sand, dust sand, silt and clay, the clay only settling with difficulty in water when this is stationary.

Analysis, or mere eye examination of the different portions obtained, may possibly afford evidence as to the refractoriness of the clay. Thus, quartz in an exceedingly fine state may act as a flux, whereas coarser particles do not have this effect.

(229) **The Impurities in Clays and their Effects.**—The impurities in clays are many, and they have a pronounced influence in many cases

upon the chemical and physical properties of the clays and their behaviour in practice.

SILICA may be present as an impurity in any one or all of three forms—viz., (a) as hydrated silica, (b) as free silica, quartz or sand, and (c) as silicates.

The free silica or quartz is the most commonly occurring form of uncombined silica in clays. It is not necessarily deleterious, since in coarse particles it may prevent cracking or excessive shrinking. On the other hand, an excess of silica may render a firebrick friable and easily corroded or eroded in the furnace. Again, being devoid of plasticity, quartz acts as a diluent when mixed with clay, makes it "short" or "lean," and reduces shrinkage on drying and firing. "Sand" occurring in clay may be quartz, quartzite, or any other mineral of a highly siliceous character. Some sands are rich in combined silica in the form of feldspar, mica, and other mineral silicates and alumino-silicates. These are detrimental to the refractory properties of the clay. This is due to the fact that such feldspathic or micaceous sands introduce alkalis (which act as fluxes) as well as silica.

The effect of silica differs according to circumstances. If it is added to pure clay, the refractoriness is reduced, but if added to a fireclay of low fusion-point the refractoriness may be improved to a limited extent. In general, the addition of silica to fireclays reduces the plasticity, shrinkage, tendency to warp, tensile and crushing strength, and the porosity in soft burned pieces; it increases the rate at which the clay can be dried, the porosity of harder burned pieces, the permeability of the clay, and the resistance to breakage due to rapid changes of temperature. When the quartz is in a finely divided state, however, some of the effects stated above may be reversed.

ALUMINA, in the free state, is not nearly so common in raw clays as is silica. The Ayrshire bauxitic clay, however, has a high alumina content, a fair proportion of which, probably 10 per cent., occurs in the free state. It is a very greasy clay, short, difficult to dry owing to the development of fine cracks, and has a high porosity. The addition of fine alumina to a clay may increase its refractoriness; when added in a combined form, however, it reduces the plasticity and usually also the refractoriness. Clays rich in alumina are viscous and do not squat so readily on softening as those poorer in alumina. In clays required to resist the action of glass, alumina must be present in a sufficiently high proportion, and attempts have been made to improve the quality of glass pots by making an interior lining more aluminous than the exterior coating. In general terms it might be said* that up to a limit not very far from the composition of kaolin, the higher the alumina content the better the clay, providing that it still possesses sufficient plasticity and that its other properties are suitable, some of which are related to physical structure rather than to chemical composition.

Studying the relation between the fusion-points and the compositions of refractory clays, Montgomery and Fulton† found that: (1) the silica-alumina eutectic curve (see Fig. 89) limits the refractiveness of clay;

* ROSENHAIN, *J. Soc. Glass Tech.*, 1917, 1, 130.

† *Trans. Amer. Cer. Soc.*, 1917, 19, 303.

(2) the drop below this eutectic line in cones depends primarily upon the amount of fluxes present; (3) as the amount of flux increases its activity increases rapidly; (4) at about 14 to 18 per cent. of alumina ($\text{Al}_2\text{O}_3 + \text{SiO}_2 = 100$) will be the maximum activity of the fluxes present; and that (5) with high silica content beyond the eutectic point, the activity of the fluxes decreases rapidly.

IRON COMPOUNDS occur invariably in clays. Those most commonly found in raw clays are iron sulphide (*pyrites*), FeS_2 , and iron carbonate

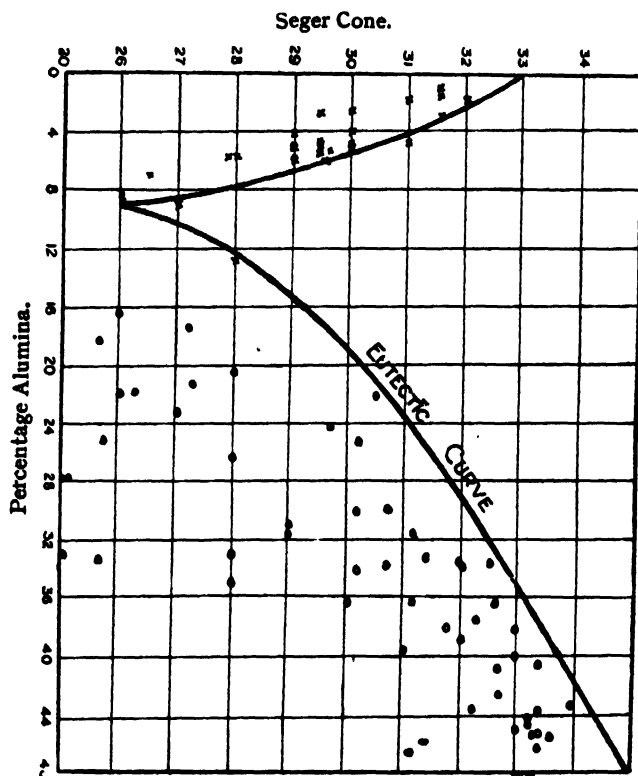


FIG. 89.—THE SILICA-ALUMINA EUTECTIC CURVE.

(*siderite*), FeCO_3 . Iron may occasionally be found as the hydrous oxide, *limonite*, $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, and the oxides, ferrous oxide, FeO , ferric oxide, Fe_2O_3 , and *magnetite*, Fe_3O_4 .

Pyrites may be distributed throughout the clay, but is usually found in the form of "nodules." Large nodules can be removed by hand picking, but small ones are left behind and, on firing, form cavities with a bluish-black slag of iron silicate, which in pots causes honeycombing. The carbonate occurs frequently in masses or as a film coating other minerals. Ferric oxide is occasionally found, whilst, on burning, all the other iron compounds may be burned to Fe_2O_3 . This oxide, so far as

refractory properties are concerned, is not seriously harmful. Ferrous oxide, though it very rarely occurs in raw clays, is frequently produced from other iron compounds in the clay by burning in a reducing atmosphere. It forms a slag with clay as indicated above, which slag fuses readily between 1100°C . and 1200°C . With silica and glass batch it forms a green coloured silicate.

Wherever *pyrites* or *siderite* is present in the clay it should be removed as thoroughly as possible when the clay is to be used for pots, since, apart from honeycombing, either may react with the formation of metallic lead from red lead in a batch. If used for bricks, it is best to burn the clay

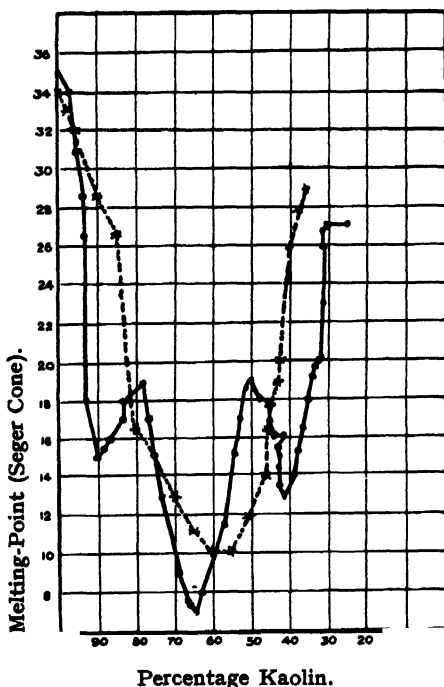


FIG. 90.—CURVES SHOWING THE EFFECT OF LIME AND MAGNESIA (DOTTED LINE) ON THE MELTING-POINT OF KAOLIN.

slowly in order to convert all the iron present to ferric oxide. The main effect of iron compounds in clays is in regard to the colour after firing, which varies from a pale cream tint to almost black.

If added to a refractory clay, iron compounds lower its fusion-point. They do not appear to diminish the plasticity of a clay, and they increase its cohesion after firing in an oxidising atmosphere, since they act as mild fluxes. Good fireclays should not contain more than 1.5 to 2.0 per cent. of iron compounds expressed as Fe_2O_3 .

CALCIUM COMPOUNDS (lime, limespar, limestone, calcium carbonate and gypsum) lower the refractoriness of fireclays as shown in Fig. 90,

which demonstrates the effect of the presence of free lime upon the refractoriness of kaolin.*

MAGNESIUM COMPOUNDS act similarly to calcium compounds and tend to reduce refractoriness. Magnesia† does not cause such ready vitrification as lime, but causes a slower softening (see also Fig. 90). Both calcium and magnesium compounds should be avoided as far as possible.

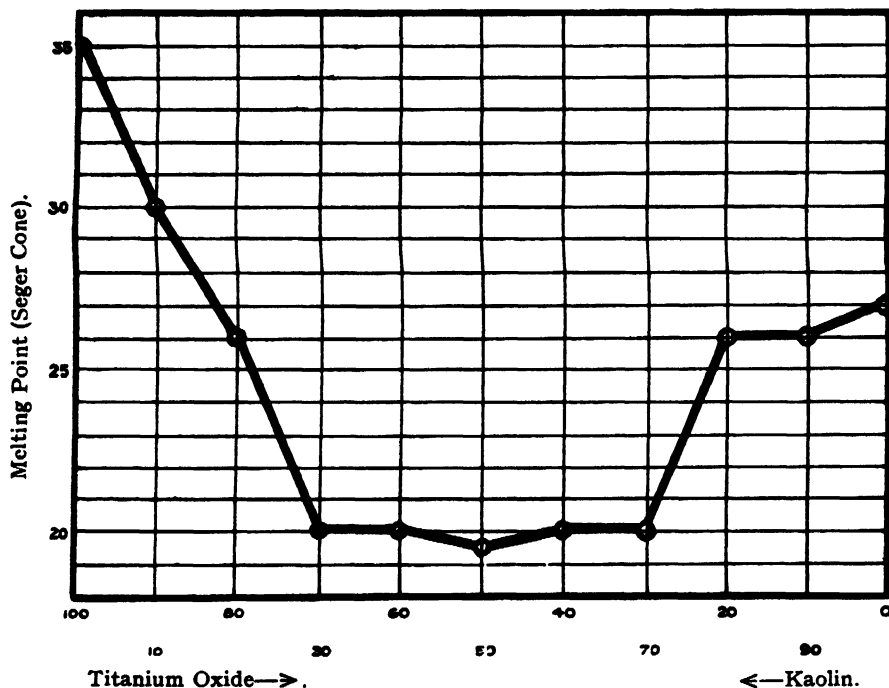


FIG. 91.—THE EFFECT OF HEAT ON MIXTURES OF KAOLIN AND TITANIC OXIDE.

THE ALKALIS, soda and potash, which occur in clay, exist largely as felspar and mica. They act as fluxes, and reduce the refractoriness, although the presence of a little alkali may increase the strength of a brick owing to a slight fluxing action. Usually the alkalis should not exceed 2 per cent. The effect of added alkalis on clays will be discussed in the section on clay purification.

TITANIUM COMPOUNDS such as rutile, TiO_2 , ilmenite, TiFeO_3 , and titanite, CaTiO_3 , cause a reduction in the refractoriness of clays. A diagram, according to Rieke,‡ is shown in Fig. 91, illustrating the effect of titanium.§ Pure titanium oxide is used occasionally as a decolouriser,||

* RIEKE, *Sprechsaal*, 1906, No. 38; 1907, Nos. 44 to 48.

† RIEKE, *Sprechsaal*, 1907, No. 17.

‡ *Sprechsaal*, 1908, 41, 406.

§ See also BRYCE, *Trans. Amer. Cer. Soc.*, 1910, 12, 533.

|| *Sprechsaal*, 1915, 48, 266.

whilst rutile has been used to impart a particular green colour to glass. The titania in clays is soluble in glass, as evidenced by the amounts found on analyses of bottle glasses.

(230) **Water in Clays.**—Clay is very hygroscopic, and if thoroughly dried it will readily absorb moisture from the atmosphere. The water held normally by raw clay is in two forms (a) that mechanically held, and (b) that which is chemically combined. The former kind, held by capillary action, may be driven out completely from the clay by heating at 110°C. , the clay, as a consequence, shrinking in volume by anything from 1 to 12 per cent. (see further under "plasticity" and "physical properties"). The chemically combined water (so-called) is only driven out when the clay is heated at a temperature exceeding 400°C. In pure kaolinite, the combined water content is about 14 per cent. Clays containing minerals like mica or limonite, which contain a less proportion of water than pure kaolinite, may have a combined water content varying from 14 per cent. down to about 3 per cent.

(231) **Organic Matter in Clays.**—Organic matter, chiefly of vegetable origin, occurs in all sedimentary clays. It may take the form of actual plant tissue, such as leaves and stems of trees, but the main type of organic matter is that of a peaty, coaly or bituminous character. All coal measure clays contain carbonaceous matter in this form, and if it reaches an amount equivalent to about 6 per cent. of the clay or shale it causes difficulty in firing.

The dark colour, grey, bluish-grey to black, of many clays is directly due to the presence of carbonaceous matter. This organic carbon is not completely removed from clays in most cases until a temperature of about 900°C. is reached (see further under "Firing of Clays").

(232) **Plasticity.**—The property upon which the utilisation of clays in the glass industry almost entirely depends is that known as plasticity. "Plasticity," according to Ries,* "is the property which many bodies possess of changing form under pressure without rupturing, which form they retain when the pressure ceases, it being understood that the amount of pressure required, and the degree of deformation possible, will vary with the material."

Clays are rendered plastic by the addition of water. Fatty oils will also produce a plastic mass with clay. Clays are lean (mild) or fat (strong) according as their plasticity is low or high respectively. The cause of plasticity is not thoroughly understood. Many theories have been advanced, but none is completely satisfactory.

Since the removal of the so-called combined water on heating a clay to a temperature of about 600°C. renders the clay incapable of being restored to a plastic state in the ordinary way, it has been held that the "combined water" has some relation to the plasticity. Fineness of grain has been advanced as a cause of plasticity, but it is an undoubted fact that the finest grained clays are not always the most plastic ones. Mellor,† however, in a comprehensive survey of the subject of the plasticity of clays, states that it is probable, other things being equal, that the

* *Clays*, p. 119.

† *Trans. Eng. Cer. Soc.*, 1921, 21, 91.

distribution of grain sizes which permits the closest packing of the particles and exposes the maximum surface area will be most favourable to high plasticity.

Molecular attraction between the particles of the clay themselves, or between the clay particles and the water used, has been cited as an explanation of plasticity, and recently, as a result of several years' work, R. F. MacMichael* concludes that: (a) the strength of clay, whether plastic, dry, or burned, is due to the molecular cohesion of the clay particles themselves; (b) water, when added to a mass of dry clay, produces a disruptive force within the mass, opposing cohesion and reducing the strength of the clay; (c) plasticity results from a balancing of the forces of cohesion and disruption; (d) fluids other than water might be used to produce plasticity in clays; and that (e) organic matter, soluble salts and colloids (except as the last-mentioned are considered to be merely fine, insoluble particles of the clay itself) are not essential to plasticity.

Notwithstanding this last statement, the colloid theory of plasticity has very many supporters. Whilst perhaps insufficiently conclusive, it does throw some light on changes of plasticity which may occur. There are some clays which unquestionably contain quite a large proportion of colloids. Such components of clays as aluminium hydroxide, silicic acid, iron oxide and organic matter may readily assume a colloidal character. Mellor† states that there is an intimate connection between the plasticity of a clay and its past history with regard to contact with water, which suggests that the clay is slowly hydrated to form a colloid, though no difference can be detected in the plasticity of a clay after removing as much of its colloidal matter as possible.

It is well known that the weathering or ageing of clays appears to increase their plasticity, and it is thought that this is partly due to the formation of organic acids caused by bacterial action or chemical processes. Without doubt, the plasticity of clays is greatly affected by the presence of organic matter—humus, tannin, etc.—and it seems to be a fact that acidity is conducive to the greatest development of this property; alkalis inhibit the plastic quality of a clay to a very pronounced extent.

In addition to this, the mechanical breaking down of the clay by the action of water-soaking and frost contributes materially towards an increase in plasticity. Increased plasticity may also be brought about by grinding the clay with water, adding weak acid or a bond of colloidal material such as silica, aluminium hydrate, etc. Plasticity can be reduced by the addition of alkaline materials such as lime-water, caustic soda or potash, and water-glass, by the addition of non-plastic material such as sand or grog (see later), or by raising the temperature to 400° C. or higher.

Just as it is difficult to discover the real cause of plasticity, so it is difficult to obtain a measure of the plasticity of clays. The practical test is the "feel" of the wet clay when handled or trodden with the feet. A clay may be said to be in its best working condition

* *British Clayworker*, 1920-21, 29, 163

† *Loc. cit.*

when it only just fails to stick to the fingers on being pressed into shapes.

Among various other methods used one may mention (a) the forcing of wet clay through a cylindrical die and determining the plasticity of the clay by the length of the thread of clay extruded before breaking as suggested by Bischof, or by its weight as suggested by Stover and Lindley*; (b) the forcing of a needle into plastic clay by means of a constant pressure; and (c) the settling of a plumb-bob into clay. Whilst the first method offers no guarantee that the point of maximum plasticity of the clay has been reached, the other two methods assume that the plasticity varies with the amount of water required to bring the clay to a plastic condition. This assumption cannot be justified, as proved by the experiments made in the Department of Glass Technology,† Sheffield University.

The preparation of cylinders of clay and the measurement of the tension required to break them, or of the compression required to reduce them to a standard length, has also been used.

Atterberg‡ describes a method of measuring plasticity which depends on the varying physical behaviour of clays with gradually increasing quantities of water. This method and modifications of it are described by C. S. Kinnison in the Bureau of Standards Technologic Paper, No. 46, issued in May, 1915.

(233) **The Effects of Heat on Clay.**—During the drying of moulded clay there is almost always a lightening of the colour and also a shrinkage in volume. The contraction in volume of the plastic clay during drying is a typical property of a colloid material, and it may show a magnitude as great as the true volume of the clay itself. This shrinkage, therefore, is a criterion of the colloidal nature of the clay, being the greater the more pronouncedly colloidal the clay is. Further, the drying shrinkage is the greater the more slowly the evaporation of the water is allowed to take place.

The first effects of heat on clay are the removal of hygroscopic moisture and the dehydration of the colloidal silicic acid. The dehydration at about 500° C. is endothermic and is associated with a marked increase in molecular volume. The clay at this temperature is decomposed into free silica, alumina, and water. It expands, but then contracts when the temperature rises above 900° C., to a mixture with a higher specific gravity due to incipient vitrification and to the change of the products of the decomposition mentioned. Le Chatelier observed an absorption of heat during the dehydration of kaolin between 550° and 650° C., and also a sudden evolution of heat on heating kaolin to 1000° C., corresponding with the change of state, which Mellor suggests is due to the polymerisation of free alumina, the polymeride being insoluble in acids.

Firing from 600° C. to 900° C. is the stage during which the carbonaceous matter is removed from the clay and the iron compounds are oxidised. Unless the whole of the carbonaceous matter is removed from the clay during this period and the iron is oxidised to the ferric

* *Trans. Amer. Cer. Soc.*, 1905, 7, 397. † FIRTH, HODKIN, and TURNER, *loc. cit.*

‡ *International Reports on Petrology*, 1911.

state, fireclay goods will be found to have a "*black core*," or, with very finely divided iron compounds, black spots. The black core may be due to (a) unburnt carbonaceous matter alone, (b) iron in the ferrous condition with practically no carbonaceous matter, or (c) both carbonaceous matter and ferrous iron. Where much iron or carbonaceous matter is present in the clay the rate of heating over the interval 600°C. to 900°C. should be slow, the kiln should be well ventilated, and oxidising conditions maintained. If black cores are formed in which some carbon remains unoxidised in the presence of ferrous iron compounds, these cores may fuse and form a slag, whilst ferrous iron compounds, heated just above 1000°C. , in contact with clay, form a fusible mass. Ferric iron compounds do not begin to fuse till well above 1500°C. The finer the texture of the clay the greater is the persistency of the black core, and, conversely, any mode of manufacture which gives an open, porous body will hinder the development of a black core.

At about 900°C. , as already quoted, an exothermic reaction occurs which may be associated with an irreversible change of a colloidal nature or with the dissociation of the aluminium silicate perhaps into $\text{Al}_2\text{O}_3, \text{SiO}_2$ and silica. In some clays, when heated to 1200°C. , sillimanite,* $\text{Al}_2\text{O}_3, \text{SiO}_2$, is definitely formed. At 1500° the clays sinter to a stone-like mass, at 1650°C. they soften, and when maintained at a temperature of about 1700°C. form a brown or grey, viscid liquid.

The external clay volume contracts as the firing temperature is raised, especially if fluxes are present, due to the effect of surface tension, until the heat intensity is sufficient to bring about practically complete closing of the pore space. The clay is then said to be vitrified. Wherever the chemical composition and the heat treatment permit, the end result is the partial elimination of amorphous substances and their replacement by crystalline forms. Thus the clay substance decomposes into sillimanite and silica.

In the case of fireclays and china clay very little vitrification occurs, but with more fusible clays an impervious clinker may be formed. Clays which vitrify readily are often valuable for binding together clays which are very friable when heated. For this reason ball clay or stoneware clay (both of which vitrify readily) are sometimes mixed with the more refractory clay used for making glass-house pots.

The Physical Properties of Clays.

(234) **The Drying and Firing Shrinkage.**—For determining the drying and firing shrinkage of a clay it is dried at a temperature not exceeding 70°C. , crushed to pass a 28 sieve, made up with water to the proper working consistency, and thoroughly pugged, or wedged by hand. The clay is then moulded, in a mould preferably made of brass, in the form of slabs four and a half inches long, one and one-eighth inches broad, and nine-sixteenths of an inch thick. On these slabs are marked vertical lines about 9 cm. apart. After drying in the air at the ordinary temperature and being removed from the mould, the slabs are further dried

* Or Mullite (see p. 175).

at a temperature of 70° C. to 80° C. for four or five hours, and finally at 110° C., until they are of constant length. The distance apart of the marks is again measured, and the linear drying shrinkage expressed as a percentage of the length between the marks on the wet test-piece. For determination of the firing shrinkages the slabs may be fired in a suitable muffle, or preferably in an electric tube furnace, to the temperature or temperatures required, if necessary being heated repeatedly at the required temperature until the length between the marks on the slab when cold is constant.

The firing should be done in an oxidising atmosphere or complications are found. With the twenty-seven British fireclays examined in the Department of Glass Technology, Sheffield University,* the drying shrinkages varied from 3.31 to 8.60 per cent., the average being about 6 per cent. The shrinkage on firing underwent little change until a temperature of at least 750° C. had been passed. The shrinkage was not continuous in all cases, and there were cases of actual expansion in that range of temperature. When the shrinkage was regular the clay was found to be highly aluminous, but not all the highly aluminous clays showed quite regular shrinkage. The shrinkages up to 1500° of these clays† varied between 7.98 and 15.11 per cent., with an average of about 12 per cent.

For use in practice a clay should have a low initial shrinkage, slowly and regularly increasing up to 750° C. or 900° C., and as small and as regular a change in the shrinkage as possible above a temperature of 900° C.

The shrinkage on firing may be reduced by using a mixture of clays, since the shrinkage is influenced largely by the quantity of combined water, organic matter, and by the texture of the clay and amount of fluxes. It may also be reduced by the addition of fine-grained quartz, grog, or other non-plastic material.

Now the contraction of a firebrick during burning is due to the resultant effect of an expansion of the silica and of the fluxes and a contraction of the clay, whilst all the particles are pulled closer together by the surface tension of the molten fluxes. This contraction is seldom, if ever, completed during the firing of the brick, and an "after-contraction" takes place when the brick is in use, a contraction which should, in practice, not exceed 1 per cent.

(235) **Porosity.**—The porosity of a clay may be defined as the volume of the pore space expressed as a percentage of the total volume of the clay. Porosity is affected by the size of grain and also by the sandy or non-sandy nature of the clay. This property has an important bearing upon the strength of a clay body and upon its resistance to shock, abrasion, erosion, slagging, strains caused by temperature changes, chemical attack by gases and liquids, and also upon its permeability and thermal conductivity.

It may be determined upon the slabs already mentioned by weighing them dry, then soaking them in water *in vacuo* for about 48 hours and weighing them suspended in water, and, finally, after wiping off the surface

* *Loc. cit*

† FIRTH and TURNER, *J. Soc. Glass Tech.*, 1921, 5, 268.

moisture, weighing in air. The porosity is then calculated by means of the following equation,

$$P = \frac{100(z - x)}{x - y},$$

where **P** is the porosity, *x* the weight of the slab (dry) in air, *y* the weight (after soaking) suspended in water, and *z* the weight in air (after soaking). By this method porosity determinations are possible only after firing the clay at temperatures of 600° C. or higher. The clays whose shrinkages have been quoted had porosities at 600° C. ranging from 18.2 to 34.2 per cent., with an average of about 27 per cent. At 1400° C. they varied from 5.2 to 31.8 per cent., and at 1500° C. from 1.4 to 29.2 per cent.

Although the most useful clay in most ways is the one with the widest range of porosity, a clay is not to be rejected solely because of a short porosity range. Amongst the above clays, those with an exceptionally high porosity were rich in alumina. Where an increase in porosity occurred between 1400° C. and 1500° C. it was due to overfiring of the clay, which caused blistering and the production of a vesicular structure.

The methods of determining porosity are receiving considerable attention at the hands of E. W. Washburn* and his colleagues.

(236) **Tensile Strength.**—The tensile strength of a clay may be measured by the resistance which the dried clay offers to being pulled apart. To obtain the highest possible results the clay must be very carefully prepared, be perfectly homogeneous in texture, free from air bubbles, laminations, and cracks. A machine is usually used for the testing such that when shot is run slowly into a loading tin, multiplying levers produce an increasing tension on the test-piece until it ruptures. The tensile strength in pounds per square inch is given by the expression—

$$\frac{\text{Weight of shot in pounds} \times \text{machine constant}}{\text{Area of the fracture in square inches}}.$$

The tensile strength of raw clays may vary from a value below 10 pounds to upwards of 400 pounds per square inch. This property of clays, particularly of fired clays, is of distinct importance in practice,† and has received much attention.

(237) **Crushing Strength.**—The resistance of refractories towards crushing *when cold* is not nearly so important as their resistance when hot. Refractories differ very considerably as regards their crushing strength, a very potent factor being the texture of the article. The presence of considerable amounts of easily fusible constituents increases the crushing strength of refractory materials when cold, but has the reverse effect when hot. Grog in excess renders the material low in resistance towards crushing, but in suitable amount and gradings increases the resistance (see further, paragraph 239).

(238) **Refractoriness.**—The refractoriness (normal refractoriness) of a clay may be determined by shaping a representative piece of the clay into the form of a cone about 1½ inches high, cementing it, together with

* See *J. Amer. Cer. Soc.*, 1921 and 1922.

† See TRAVERS, *J. Soc. Glass Tech.*, 1919, 4, 138.

Seeger cones, on a refractory disc, and then firing in a Hirsch or similar electric furnace. The temperature of the furnace should be increased at the rate suitable for Seeger cone measurements (see p. 290), and the temperature at which the test-piece bends over, squats or shows sign of fusion is taken as the softening point, and is deduced from the Seeger cone which bent down last.

In Table LXXXIX. are given the softening temperatures of certain refractory products as determined by C. W. Kanolt,* and certain estimated fusion temperatures in Table XC.

Refractoriness is reduced by fluxes and composition changes, as already indicated (see pp. 290 to 294).

TABLE LXXXIX.—SOFTENING TEMPERATURES OF REFRACTORIES.

<i>Refractory.</i>	<i>Number of Samples.</i>	<i>Temperature of Visible Flow.</i>
		<i>Degrees C.</i>
Fireclay brick	41	1555—1725
Bauxite	8	1505—1785
Silica	3	1700—1705
Chromite	1	2050
Magnesia	1	2165
Kaolin	1	1735—1740
Bauxite.. ..	1	1820
Bauxitic clay	1	1795
Chromite	1	2180
Alumina	—	1970
Magnesite	—	2500

TABLE XC.—FUSION POINTS OF REFRACTORIES.

<i>Substance.</i>	<i>Fusion Point.</i>
	<i>Degrees C.</i>
Pure china clay	1830
Firebricks	1400—1650
Zirconia	2560
Pot clay (Dralle), suggested limits	1580—1825

(239) **Refractoriness under Load.**—One of the most important physical properties of clays when in commercial use, is the refractoriness under load. When under compression, as in a furnace structure, the refractoriness or resistance to fusion of a clay is reduced, and the reduction of the fusion or softening point increases with the pressure to which the clay is subjected.

A rectangular block presenting a surface of 4 square inches to the load is used for testing the refractoriness under load. This block is placed centrally on a refractory support in the inner tube of a Hirsch

* *Trans. Amer. Cer. Soc.*, 1913, 15, 167.

furnace with Seger cones round it. Generally a constant pressure is brought to bear on the test-piece by means of a mechanical device outside the furnace, and when, on heating, the squatting of the test-piece occurs the temperature is obtained from the cones as before.

Bodin* obtained results for various substances as shown in Table XCI., but he actually determined the load required to crush or squat the material after firing to any particular temperature and whilst it was retained at that temperature.

TABLE XCI.—CRUSHING STRENGTHS OF REFRACTORIES.

				<i>Crushing Load in Kilograms per Square Cm.</i>				
<i>Refractory.</i>				<i>At</i> 20° C.	<i>At</i> 800° C.	<i>At</i> 1000° C.	<i>At</i> 1300° C.	<i>At</i> 1500° C.
Clay A	195	125	105	740	40
" CL	920	555	575	360	65
" P	1,110	485	1,755	115	20
Bauxite	395	270	715	55	20
Corundum	790	530	615	310	30
Carborundum	415	425	585	150	70
Silica brick A	277	—	—	—	116
" " B	276	—	—	—	27
" " C	244	—	—	—	53
" " D	171	—	—	—	1
" " S	180	90	80	60	40
" " V	240	125	185	160	100
Fused quartz	2,550	1,040	780	1,670	100
Impure zirconia	395	275	345	90	10
Magnesia brick (Eubœa)	260	265	230	110	5
" " (Styria)	450	295	190	155	30
Chromite brick	450	450	425	215	75

In general, the higher the temperature to which a fireclay brick has been fired before use, short of over-firing, the greater will be its refractoriness under load.

Mellor and Emery† found that the refractoriness of a fireclay under load diminished as the load increased in accordance with the rule—

$$\text{Refractoriness} = Ce^{-kw},$$

where C was the refractoriness (normal), e was the base of Napierian logarithms, k was a constant characteristic of each fireclay, and w was the load in pounds per square inch; further, that the sensitiveness of a fireclay to load was greater the greater the alumina content, and less the greater the silica content. Taken generally, the smaller the proportion of fine grog to clay, the higher will be the refractoriness under load. There is also indication of the possibility of a maximum effect being obtained with a particular proportion of fine grog and clay, and that this

* *Brit. Clayworker*, 1921, 80, 123.

† *Trans. Eng. Cer. Soc.*, 1916, 15, 117; 1918, 17, 360.

maximum will vary with each clay. Similar remarks apply to the medium and coarse sizes of grog, but the effects are less marked.

(240) **Specific Heat and Heat Conductivity.**—Specific heat has already been defined in Chapter III. Bradshaw and Emery* give the figures quoted in Table XCII. for the specific heats of various refractory materials at different temperatures.

TABLE XCII.—SPECIFIC HEATS OF REFRACTORIES.

<i>Temperature.</i>	<i>Silica Brick</i> (96.6 per Cent. SiO_2).	<i>Silica Brick</i> (84.65 per Cent. SiO_2).	<i>Firebrick</i> (59.2 per Cent. SiO_2 ; 35.3 per Cent. Al_2O_3).	<i>Zirconia</i> (99 per Cent. ZrO_2).
<i>Degrees C.</i>				
600	0.226	0.228	0.228	0.137
1000	0.263	0.262	0.265	0.157
1200	0.282	0.283	0.284	0.167
1400	0.293	0.295	0.297	0.175

It will be noticed that in the case of each material the specific heat increases distinctly with rise of temperature, and that the specific heats of the silica and fireclay bricks quoted are very similar.

The effective insulation of furnace walls, the transfer of heat from outgoing to ingoing gases in regenerators and from the furnace to the batch within a pot, all depend upon the conductivity for heat of the refractory materials. The conductivity varies with the chemical composition, porosity, grain size, and firing temperature of the material, and also upon the difference in temperature between its opposite faces.

R. H. Hörning† determined the heat transmission of a number of refractories, and some of his results are given in Table XCIII.

TABLE XCIII.—HEAT TRANSMISSION BY REFRACTORIES.

<i>Material.</i>	<i>Temperature Difference Between the Faces in Degrees Fahrenheit.</i>													
	200	300	400	500	600	700	800	900	1000	1100	1200	1300	1400	1500
Silica brick	123	127	132	136	139	142	145	148	151	153	154	156	158	159
No. 1 fire-	57	57	62	66	70	74	77	81	83	85	86.5	87	87.5	87.5
brick														
Re-pressed,	24	25	26	26	26.5	27	27.5	27.7	28	28.1	28.2	28.5	28.5	28.5
burned														
Kieselguhr														
brick														
Nonpareil	13	14.4	15.6	16.8	17.8	18.8	19.6	20.1	20.6	21.0	21.4	21.7	22.0	22.2
insulating														
brick														

The figures quoted are given in terms of British thermal units transmitted per twenty-four hours, per square foot area, per degree Fahrenheit difference in temperature between the opposite faces, per one inch thickness.

(241) **The Purification of Clays.**—One of the best methods of effecting the purification of any clay is to suspend it in water, when the addition of traces of alkaline substances such as caustic soda, NaOH , sodium carbonate, Na_2CO_3 , or sodium silicate, Na_2SiO_3 , causes the clay particles to remain in suspension over a long period, whilst the coarser grains of mica, pyrites, felspar, free silica, and other impurities settle through the liquid. This holding of clay in suspension by means of alkalis is known as "deflocculation." The clay suspension may be poured off from the settled impurities and "flocculated" or coagulated again by the addition of acid.

The disadvantages* of this method are that certain fine impurities remaining in suspension are carried down by the clay, only partial purification is obtained, the physical state of the clay is entirely altered, and it is left in a form difficult to collect and dry.

An interesting phenomenon, however, in connection with clay suspensions is the possibility of the electrical deposition of the clay particles, upon the positive electrode, by a direct current against a flow of water away from the electrode. By immersing two cylindrical electrodes in the clay suspension, the clay particles move towards the anode and adhere to it in a coagulated mass, whilst the water, carrying with it even the finest impurities, moves towards the cathode, leaving the clay in a semi-dry state. A machine with an anode in the form of a cylinder five feet in length and two feet in diameter is said to produce about 1,000 tons of pure clay per annum. The clay leaves the machine in the form of a blanket from one-quarter to one-half an inch in thickness, containing only 25 per cent. of water, and in a form which readily admits of drying. Unfortunately the process is too costly for general application to fireclays in this country, though it has been used to some extent in Germany, where good fuel is dearer and ordinary methods of drying are more expensive.

Sintering occurs with clays purified with the aid of alkalis at lower temperatures than with raw clays, thus saving fuel. The lower sintering temperature and the higher fusion-point result in articles showing little further contraction after burning. The reduction of the sintering temperature is stated to be as much as 300°C . for low grade clays, whilst bricks from some clays after osmosis are better burnt at 1100°C . than bricks from raw clays burnt at 1300°C .

(242) **The Effects of Grog.**—Grog is the term applied to burned and broken-up clay or potsherds used for admixture with raw clay for the manufacture of bricks, blocks, and glasshouse pots. Opinions differ as to which is the better form of grog. Harrop† recommends raw clay burnt and ground specially for grog, for the reason that such grog is harder, denser, and more angular in grain than either ground potsherds

* HIGHFIELD, ORMANDY, and NORTHALL-LAURIE, *J. Roy. Soc. Arts*, 1920, 68,

514.

† *Trans. Amer. Cer. Soc.*, 1916, 18, 165.

or prepared clay previously shaped into blocks, fired and ground for grog.

The higher the temperature to which the grog has been fired before use the more satisfactory will be its effects. Black-cored grog should never be used.

The grog should be proportioned so that the smaller sizes fill the voids between the larger particles, giving a maximum density and strength.

Grog for glass pots and similar bodies may contain too much fine or intermediate sized material, causing a low mechanical strength and cracking on drying. It is not, however, an advantage to sift out the whole of the fine dust from grog before mixing it with the clay, since the fine dust, to a greater extent than the larger particles, reduces the drying and firing shrinkage of the clay and so hinders it from drawing away from the larger grog particles and leaving cracks. The finer portions of the grog, on burning, combine readily with the raw clay and form a dense, non-porous body, very suitable for glasshouse pots. The coarser particles of grog act as a skeleton or frame and give strength to the clay body, and also assist in rendering it less sensitive to temperature changes.

The proportion of grog used is also important, but, in general, the greater the amount of grog the raw clay can take up without causing difficulty in moulding and in cracking on drying and firing, the better will be the final product. As the proportion of grog used increases, the shrinkage on drying and firing tends to decrease. The strength of the fired product is increased so long as an excess of grog is not used, whilst the porosity increases. The possible rate of drying and firing is therefore increased and a saving in fuel results. On the other hand, excess of grog renders the product too porous and friable.

The amount of grog to be used in pot-making varies with a number of factors, such as the size of the pot, the temperature employed, the treatment the pot is to receive when in use, and on a human factor. Larger proportions of grog should be used for the bigger pots and when the temperature employed is high. If the pot is to be taken from the furnace, emptied, and returned to the furnace, as in the production of plate glass, then the largest possible proportion of grog should be used. The human factor may be illustrated by the fact that German pot-makers frequently use higher proportions of grog with Stourbridge clays than are generally used in this country.

The following suggestions are in accord with the practice in many works:

<i>Grog Size for Pots up to 40 Inches Diameter.</i>	<i>Grog Size for Pots up to 70 Inches Diameter.</i>
All through 10-mesh.	All through 8-mesh.
30 per cent. on 16-mesh.	50 per cent. on 16-mesh.
Percentage of grog (by volume) 20 to 33.	Percentage of grog (by volume) 25 to 50.

The actual proportions of grog must vary with the plasticity of the raw clay, which should be ground as fine as possible. Grog larger than 8-mesh is not generally favoured for pots, but some 4-mesh grog can be used with advantage when the pots are required to withstand rapid changes of temperature. For blocks, grog up to half an inch in diameter has been used.

CHAPTER XXIII

THE MANUFACTURE OF GLASSHOUSE POTS AND BLOCKS

(243) **Blocks.**—Fireclay blocks, intended for use as “flux-line blocks, should be made of the same clay mixture as pots, for a dense structure is necessary. Ordinary blocks, whilst they do not require to be of quite the same quality, should nevertheless approach perfection as nearly as possible, in consequence of modern working temperatures and high rate of production.

After being mined, the clays are weathered. Weathering breaks up the clay, tends to increase plasticity, and reduces the quantity of impurities. The analysis given in Table XCIV. illustrates the value of weathering upon composition.

TABLE XCIV.—THE EFFECT OF WEATHERING UPON THE COMPOSITION OF CLAYS.

				<i>Before Weathering.</i>	<i>After Weathering.</i>
				<i>Per Cent.</i>	<i>Per Cent.</i>
SiO ₂	64.62	64.70
Al ₂ O ₃	21.65	22.90
Fe ₂ O ₃	1.48	1.30
CaO	1.98	1.01
Alkalis	1.62	0.75
Moisture, etc.	8.52	9.52

The clay is then ground in a mill and the required mixture of strong, mild, or medium material made according to the class of article required. This blending of clays of different qualities is one of the most important considerations in the manufacture of refractory materials for glassworks, and it is very necessary that thorough investigations shall be made of the possibilities of such blending.

Grog is next added in varying proportions, about 30 or 40 per cent. being used for large blocks and from 15 to 20 per cent. for ordinary bricks. The mixture is wetted up, mixed thoroughly, and, for the best ware, is then allowed to mature. After moulding, drying is carried out very slowly, in order to prevent cracking, and then the firing is proceeded with at a rate which ensures a thorough burning of the block, leaving no under-burned interior or black core. The firing temperature should be as high as that likely to be encountered in practice.

(244) **Pots.**—For glasshouse pots the clay is prepared in a manner very similar to that used for blocks and bricks, but in any case the clay should be carefully hand-picked as free from pyrites as possible. The grog is carefully graded to suit requirements, and here again much experimental work requires to be done on particular clays in order to obtain the very best mixtures and proportions for all purposes. The grog is often prepared from the same mixture as the raw clay.



FIG. 92.—TREDDING CLAY.

(This and succeeding illustrations up to and including Fig. 105 are reproduced from photographs taken by Mr. F. Winks, B.Sc.Tech., with the kind permission of Messrs. Beatson, Clark and Company, Ltd., Rotherham, and Mr. F. Mayfield, pot-maker.)

After thoroughly mixing the grog and raw clay water is added to render the mixture plastic, after which it is allowed to stand for a considerable time, about three months being satisfactory. Periodically the clay is "turned over" and trodden with the feet, and, on nearing the best working consistency, thoroughly trodden and mixed to remove all the air bubbles. The method at this stage is to dig out the plastic clay

with a spade and project it forcibly on to a clean floor until an approximately circular heap of clay is obtained, about 4 feet in diameter and 12 to 18 inches in thickness. Then a man mounts the mass and treads (see Fig. 92) it down to a thickness approaching 9 inches. By means of the spade slabs are cut from the outside edge and brought forcibly down upon the middle of the mass until the original thickness and diameter is approximately restored. The process is repeated until the clay is thoroughly homogeneous and ready for the pot-maker. The tramping



FIG. 93.—MAKING THE BOTTOM OF A POT.

of the clay may be done with the bare feet or whilst wearing wooden clogs, but the former method is more effective, whilst the man's bare feet become very sensitive to the "feel" of the clay, and he is able to judge very accurately when the clay has reached its best working consistency.

The pot-maker then takes the clay in rolls and, breaking portions off the rolls, throws them forcibly upon a board and spreads the clay out by a forward pressing motion with the heel of the hand and a reverse, drawing motion with the finger-tips (see Fig. 93). The board is of a

size to accommodate the pot bottom and of strength requisite to bear the weight of clay required for the bottom. It is fitted with two pairs of handles so that the whole can be lifted. When the bottom reaches the required thickness, usually from 3 to 6 inches, the board is lifted, turned over, and the pot bottom reversed and laid upon a second board (see Fig. 94). This second board, upon which the pot will remain on completion, is covered with a thin layer of grog, which enables the pot bottom to crawl or shrink easily during drying. The first board is cut



FIG 94.—THE POT BOTTOM REVERSED.

away from the clay by means of a large band-saw, leaving a pot bottom of the required thickness and shape upon the second board (see Fig. 95). The edges of this slab of clay are covered with cloths to prevent too rapid drying (see Fig. 96), and the bottom is left to dry a little before the building of the sides of the pot is commenced. The length of time of this drying depends upon size, upon the nature of the clay, and upon the skill and judgment of the pot-maker. After a certain number of bottoms have been "laid down," a start is made upon the sides of the

first pot. The cloths around the edge are removed and the edge is wedged up between the hands so that a thin rim of clay about 3 inches high rises round the bottom (see Fig. 97). Rolls of clay are prepared about 7 or 8 inches long and 2 inches in diameter. The pot-maker takes a roll of clay in his right hand, and by a to-and-fro motion of the hand and a drawing of the forefinger along the side of the rim, the roll of clay is spread upon the outside of the rim. Each movement of the hand can be traced in Fig. 98, whilst below the last course can be seen parallel



FIG. 95.—THE POT BOTTOM AFTER REMOVAL OF ORIGINAL BOARD.

markings produced by the pot-maker stroking his fingers along the last portion of clay put on the side. This serves to spread the clay, break up any possible air-bubbles, and facilitate drying on the surface before the next layer of clay is put on. Each time the pot-maker puts on a layer of clay to form the walls of the pot, the thickness of the wall increases by about one-quarter of an inch. Supporting the inner portion of the pot wall with his left hand against the pressure applied with his right hand, the pot-maker proceeds round and round the pot wall,

working from the bottom upwards until a series of layers of clay have been superimposed one on the other forming the required thickness (from 2 to 4 inches) of wall, and standing some 10 or 12 inches above the board. In Fig. 99 the successive layers of clay can be clearly seen by looking at the top of the partly built pot wall. The position of the pot-maker's forefinger drawing the clay along during the working of these courses is also clearly shown. Fig. 100 gives another view of the process, and also shows the grog particles sprinkled upon the board. The top of the rim of clay is now wedged up between the palms of the hands, compressing all the separate layers one into the other, the whole

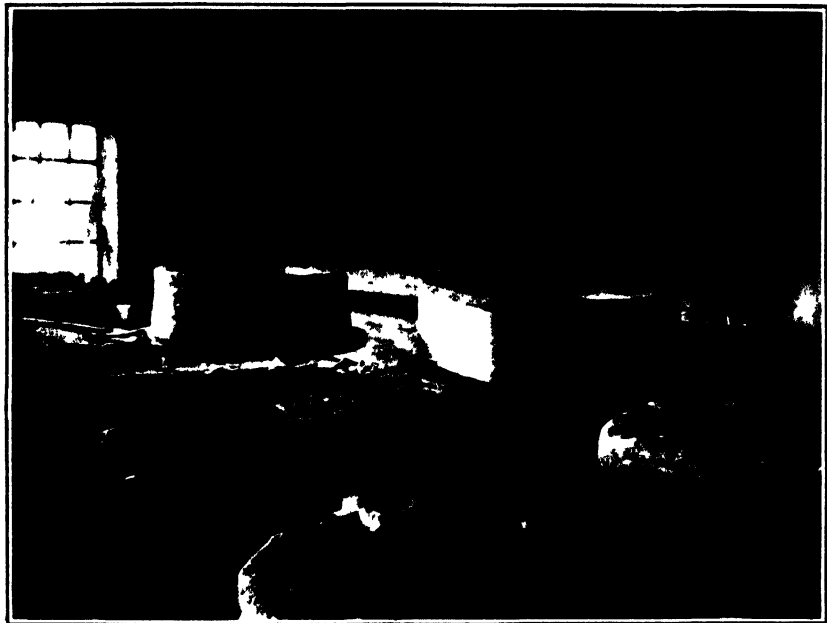


FIG. 96.—EDGES OF BOTTOMS COVERED WITH CLOTHS.

is stroked over with the fingers as indicated before, covered with cloths and left to dry slowly. The side of the pot is rendered perfectly smooth by stroking in one direction with a flat piece of wood.

When this first section of the pot wall is sufficiently dried to support the next section the latter is built up in the same way. Three or four sections, each from 8 inches to 12 inches high, are necessary in order to raise the pot wall to the height of the shoulder. The skill of the pot-maker is again in evidence here. One section must not be allowed to dry too much or the section above will not "weld" on to it thoroughly and a join will be left which may prove a source of weakness when the pot is in use. If the clay is not sufficiently dry to support the succeeding section then the shape of the pot suffers. The method here described,

of putting the clay on in superimposed vertical layers, goes a long way towards eliminating any trouble from "joints." Where the clay rolls are pressed down in horizontal layers, by means of the thumb, to form the walls, the likelihood of cracks due to uneven drying is much greater. The shoulder of the pot is now turned to the stage shown in Fig. 101. The method of building is as described before, whilst the symmetrical turning of the shoulder depends upon the art of the pot-maker. After drying sufficiently to support itself a further addition to the "crown"

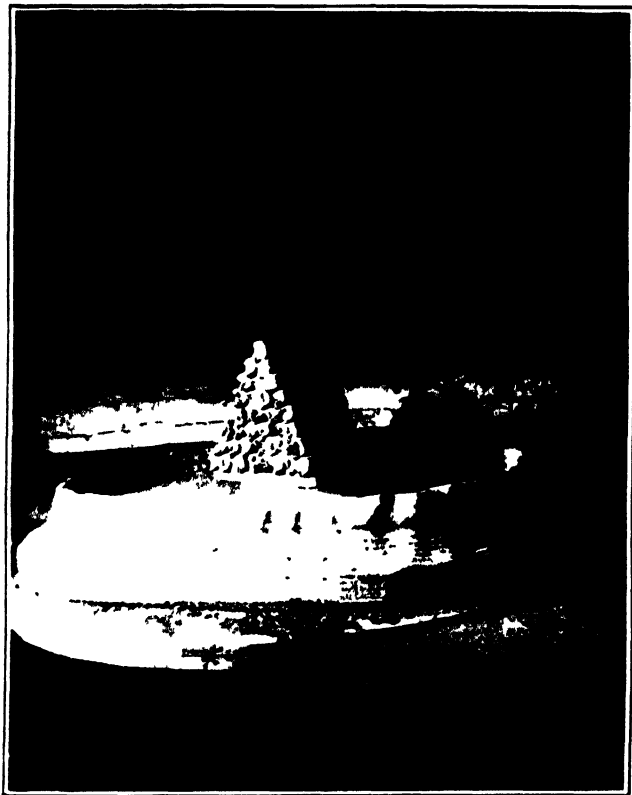


FIG. 97.—THE COMMENCEMENT OF THE POT WALLS.

of the pot is made, bringing it to the stage shown in Fig. 102. Another short period is allowed for drying, and the hole in the top of the pot is built up into the form of the narrow mouth of a large jar. It may then be closed by pressing together, or the pot-maker, inserting a tube, may blow air into the interior of the pot, closing the opening in the pot roof as he withdraws the tube (still blowing). The air in the interior of the pot, whether under pressure or not, serves to support the crown. Opinions differ as to whether it is an advantage or not to blow air into

the pot to increase the pressure. If the pot is left under pressure for too long a period, the crown is likely to crack as it dries, but if the pressure is released at the proper time by poking a hole in the pot mouth (see Fig. 104) the pressure method produces a better shaped crown. Without pressure, the crown always tends to sink a little, and may leave a rather sharply turned shoulder.

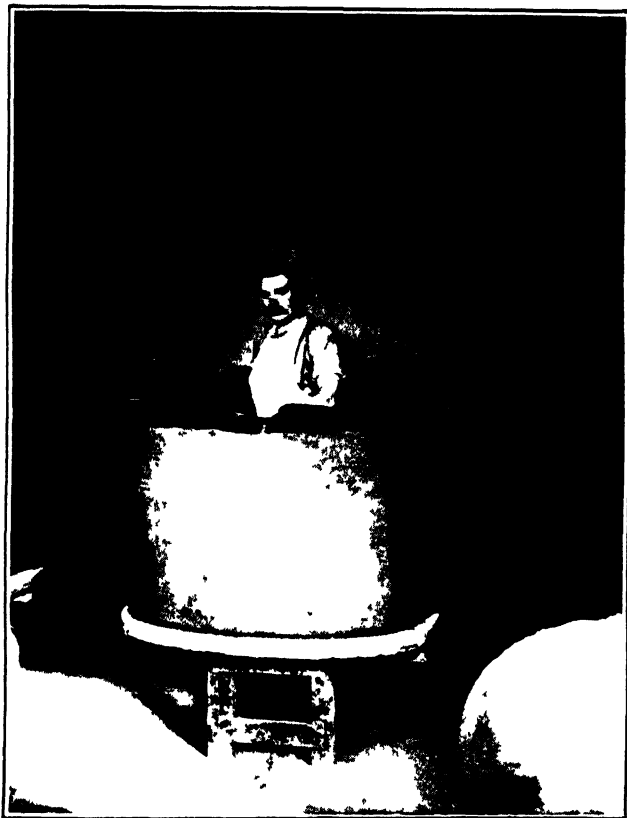


FIG. 98 —POT BOTTOM, START OF WALLS, AND CLAY ROLLS

The pot has now the appearance of a large vertical-sided beehive with no opening. Having measured the correct height for the pot mouth, the pot-maker spreads rolls of clay on the pot side to form a resting-place for a wooden pattern used to construct the pot mouth Fig. 103 shows the pattern in position. The mouth is then built up round the prepared shape, the clay being worked on as for the walls, and when the pattern is removed the pot is left as shown in Fig. 104. After a short drying period the inside of the pot mouth is cut away, the crown smoothed over, and the whole of the outside of the pot, leaving the finished article as shown in Fig. 105.

Another method of preparing the crown is described by Grafton.* He uses a little stiffer clay than has been used for the walls of the pot, and to finish the crown in one working builds the pot up to a foot or so higher than it will be at the finish, and then beats it down to the desired shape. The air inside, becoming compressed, carries the weight of the



FIG. 99.—SUCCESSIVE LAYERS OF CLAY IN POT WALLS.

crown. Considerable skill is necessary to beat down a crown properly without caving in the entire pot. The hood (or pot mouth) is put on as described, cut out, and a small boy introduced through the pot mouth to turn off the inside of the crown to the correct dimensions.

During the whole of the building process the temperature of the room should be kept constant at about 60° F. to 70° F., and the same temperature maintained until the pots are thoroughly dry and ready for use. Dust and contamination of the clay in any way must be very strictly guarded against.

Pots of the open type are frequently made in a wooden mould,

* *J. Amer. Cer. Soc.*, 1920, 3, 653.

the clay being pounded and wedged into shape and to the required thickness and height, the construction of the pot being completed in a day.

(245) **Slip-Casting of Pots.**—The casting of pots is becoming more common. In this process, first devised by Weber, the clay is mixed or



FIG. 100.—SUCCESSIVE LAYERS OF CLAY IN POT WALLS.

pugged and fed into a blunger. Water containing a small proportion* of sodium carbonate or sodium silicate or both is run into the blunger and the rotating blades of the blunger rapidly convert the clay into a mobile slip. The slip is run from the outlet of the blunger into a plaster-of-paris mould containing a core of similar material. Mould and core absorb moisture, leaving a pot of uniform and firm structure. Great care must be taken to have the slip of the correct consistency†

* About 0.2 to 0.3 per cent. of the weight of the dry clay.

† J. W. WRIGHT and D. H. FULLER, *J. Amer. Cer. Soc.*, 1919, 2, 659, recommend a specific gravity of 1.90 to 1.95 (see further, p. 321).

or the pot will be found to have walls which are hollow. Cast pots can be made containing a larger proportion of grog than those made by hand, having a greater uniformity of texture and a greater density. The process is quicker than the hand process, and requires unskilled labour only.

For covered pots, the crown is cast separately from the body, and the two united when they are still moist but firm enough to stand without losing their shape.



FIG. 101.—THE TURNING OF THE POT SHOULDER.

(246) **Vacuum Casting of Pots.**—Allen* has patented a process for the vacuum casting of glass pots. For open pots a reinforced plaster mould is used without a core, and surrounded at a little distance by an iron casing. Slip is poured into the mould and the vacuum maintained in the space between mould and casing. The suction produced by the vacuum causes a deposition of clay upon the inner surface of the mould, the deposit

* *J. Soc. Glass Tech.*, 1919, 3, 78.

increasing in thickness with time. The process may be applied to cored moulds and to the casting of covered pots. Allen claims that pots cast by the vacuum process dry much more quickly than any other type, and can be made ready for the pot arch in a week.

(247) **The Sizes of Pots.**—Pots are made of various sizes and shapes.* The dog-house pot, the building of which has been described at length, may be circular or oval, having a diameter up to 6 feet. In Fig. 106

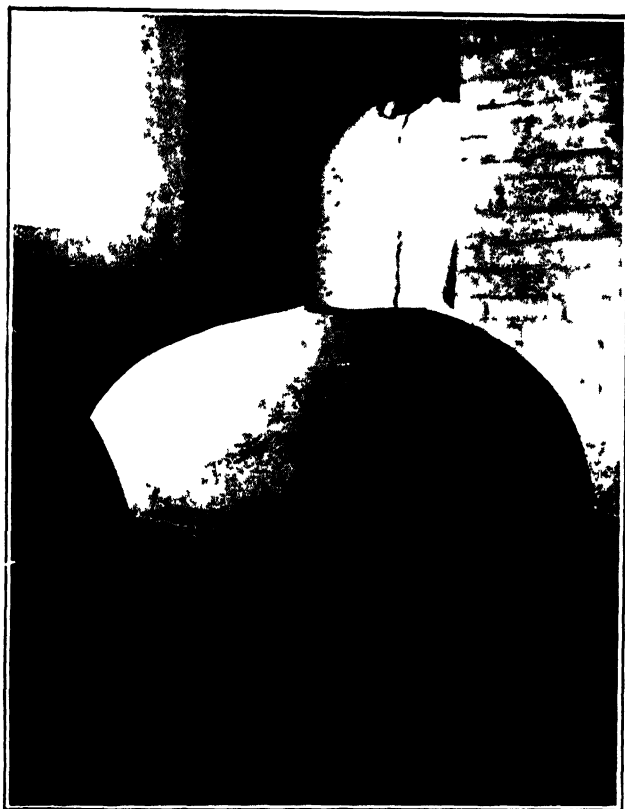


FIG. 102.—THE CROWN OF THE POT ALMOST COMPLETED

are shown other forms of pots, (a) a "skittle pot," used in the furnace in an inclined position to facilitate gathering of the glass, and (b) a "potette," used fairly frequently in tank furnaces to obtain glass free from unmelted material and at a lower temperature than the main bulk of the glass; the glass flows into the potette through a slit near the bottom.

Most frequently the height and greatest diameter of the pot are made equal, the thickness of the bottom being from one-tenth to one-twelfth of

* SEARLE, *loc cit.*

the greatest diameter and the thickness of the sides from one-fifteenth to one-twentieth of the greatest diameter. The dimensions of a pot naturally depend to some extent upon the purpose for which it is to be used. For example, pots for sheet and plate glass need to be stronger and heavier than those required for table ware. Extremely thick pots do not fail so quickly owing to corrosion, but are difficult to dry and heat up without cracking. Since the heating is done from the outside, the very thick pot necessitates the use of an excessive amount of fuel.



FIG. 103.—PATTERN IN POSITION FOR SHAPING THE POT MOUTH.

in order to obtain such a temperature within as will successfully melt the batch and plain the glass. Whatever its thickness, once the inside of the pot is badly corroded the glass tends to be cordy and stony. Medium thicknesses are therefore advisable. Wide and shallow pots are, in general, better than narrow and tall pots both for making the glass and working it out.

The side walls may be tapered at the shoulder and the crown made thicker than the sides, but it is doubtful whether this offers any advan-

tage whatever. Pots which are narrower at the bottom than the top are less likely to bulge at high temperatures.

In the United States 6-foot pots have been, and are, used even for electric lamp bulb manufacture. For bottle glass, pots may be 3 to 4 feet in diameter (if oval the largest diameter from front to back may be 4 feet 6 inches), and 2 feet 6 inches to 3 feet 6 inches high, with bottoms and sides in proportion. Those for special coloured glasses, and optical glasses, are smaller still, having a diameter of from 20 to 40 inches.



FIG. 104.—PATTERN REMOVED FROM THE POT MOUTH.

Baldermann* gives the following dimensions of open pots as being very satisfactory for rapid and economical melting: 1.51 metres internal diameter at the top, 1.41 metres at the bottom, 0.42 to 0.82 metre in depth, and a wall thickness of from 90 millimetres to 120 millimetres.

(248) **Special Pots.**—Since optical glass must be made free from colour, striæ, and any other blemishes, it follows that the pots in which it is made must be carefully constructed of the very best and purest

* *Sprechsaal*, 1920, 53, 2 and 11.

materials. The lack of good pots has led to considerable investigation. However, it is only intended to mention here two methods adopted for obtaining particularly resistant pot bodies.

A. V. Bleininger* describes the manufacture of pots with a composition akin to that of a hard porcelain, since other clay mixtures contained too



FIG. 105.—THE FINISHED POT.

great a proportion of iron. The grog used is obtained from the waste bisque of white-ware potteries, which corresponds to the general composition of—

35	per cent.	kaolin.
15	..	ball clay.
14	..	felspar, and
36	..	flint.

The white granite bisque softens at about cone 30 and possesses, on account of the high flint content, excellent "standing up" qualities

* *J. Amer. Cer. Soc.*, 1918, 1, 15.

under the pressure exerted by glass in the pot at such high temperatures as 1475°C . Porcelain bisque is not sufficiently refractory for this purpose, but may be used instead of the felspar introduced into the pot mixture. The white-ware bisque should be clean, and too great a proportion of fine material (< 80 -mesh) should not be used. If the grog be too fine it

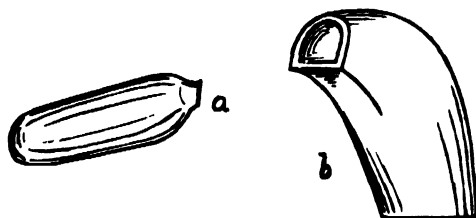


FIG. 106.—(a) A SKITTLE POT; (b) A POTTERE.

may cause serious cracking of the pots during cooling. This defect is due to vitrification, facilitated by the fine particles of grog and the resulting homogeneous porcelain structure. In satisfactory pots, the grains of grog should still retain their identity as shown by their possessing sharp outlines. The actual mixture used for building the pots is—

American white-ware bisque through 10-mesh	..	35	per cent.
Pot shell (from old porcelain type pots)	..	10	"
Felspar	3	"
Flint	4	"
Tennessee ball clay, No. 5	..	15	"
Illinois bond clay	..	5	"
Kaolin	28	"

The mixture is tempered in a wet pan, aged for a month, treading dispensed with, and the pots built by hand in the usual way.

For pots made by casting, Bleininger gives the following mixture:

American white-ware bisque	48	per cent.
Plastic bond clay	23	"
Kaolin	24	"
Felspar	5	"

The slip is composed of 80 per cent. of the above mixture with 20 per cent. of water containing 0.2 per cent. of a mixture of equal parts of sodium carbonate and sodium silicate, calculated in terms of the dry weight of the dry mixture.

Wright and Fuller* give three mixtures for making porcelain pots similar to those already described. They found that the water content of the slip should be between 22 and 25 per cent. of the dry weight of the materials, and the specific gravity of the slip 1.90 to 1.95. The amount of electrolyte varied from 0.2 to 0.33 per cent. of the weight of dry materials, and the best ratio of sodium silicate to sodium carbonate was 4 : 3.

It is important in using the porcelain type of pot to raise the temperature of this to not less than 1400°C . before the charge of batch is

* *Loc. cit.*

introduced, in order that the body may become vitrified. The temperature is then lowered somewhat and the batch filled on. If this is not done the benefits of the porcelain structure are lost and the pot may corrode as much as, or more than, does the ordinary pot.

The second method of manufacture of pots, making them less corrodible by molten glass, particularly by a heavy lead-potash glass, is to develop an inner lining to the pot. S. R. Scholes* used a refractory clay body composed of 90 per cent. of ordinary clay pot batch and 10 per cent. of felspar. A lining of this mixture was applied to the pot during building in the ordinary way so as to give a half-inch thickness up to the metal line and continued 8 inches above that in gradually diminishing thickness. On firing, a dense, vitrified interior was obtained. Lined pots could be fired as readily as ordinary pots, and the only difficulty experienced was the formation of cracks in the lining, owing to the sudden cooling of the dense material by the introduction of cold batch.

(249) **The Firing of Glass Pots.**—The ordinary drying of glass pots has been already mentioned. In some factories "humidity drying" is employed. Brownlee and Gorton† state that where temperatures under 80° F. are employed, pots can be dried safely in five weeks after completion by maintaining a minimum relative humidity of 65 per cent., and certain evidence showed that better pots were produced by preserving a constant humidity of 65 to 70 per cent. from start to finish.

Following the drying period the pot requires to be slowly heated up prior to being introduced into the furnace. This preliminary firing of the pot is carried on in specially constructed furnaces called "pot arches" (see p. 385), and is a very critical period in the life of the pot. Too rapid or uneven heating may result in the destruction of the pot either in the pot arch or, what is infinitely more serious, in the furnace after being filled. A previous investigation of the drying and firing shrinkages, porosity and density changes of the pot-clay mixture will indicate the periods during which the rate of heating may be rapid or where it must be exceedingly slow. Where rapid changes in size or density occur it is obvious that the rise of temperature must be slow, but where only slight or very regular changes occur the heating may be much quicker. Careful control of the pot arch temperature by means of recording pyrometers is necessary, whilst the impinging of flames upon the pot must be avoided.

Heating is commenced with a slow fire and smoky flame. The pot is raised in temperature from normal to about 1200° C. in from five to seven days. The following heating schedule has been found, in America, to be useful for the largest and densest pots:

		Degrees C.	
After	24 hours—	75.	
"	48 "	—	120.
"	72 "	—	371.
"	96 "	—	596.
"	120 "	—	816.
"	144 "	—	1025.
"	168 "	—	1160.

* *J. Amer. Cer. Soc.*, 1920, 3, 498.

† *J. Amer. Cer. Soc.*, 1921, 4, 97.

Brownlee and Gorton* suggest, without reference to size, the following as a useful guide in raising the temperature of a pot:

<i>Internal Temperature in Degrees F.</i>	<i>Time Needed (Hours).</i>	<i>Rate of Heating (Degrees per Hour).</i>
80 to 400	40	8
400 „ 900	41	12
900 „ 1500	60	10
1500 „ 2200	35	20

After retention of the pot at a temperature of between 1100°C . and 1200°C . for a period lasting up to 30 hours it is customary to transfer it to the furnace. The pot at this stage is in a condition such that the grog and bind clay of which the pot is made can still be clearly defined. It is most advisable, before any batch is filled into it, that the pot should have reached what may be termed the "vitreous" condition—a condition such that the pot body appears to be quite homogeneous. This condition is usually attained by heating the pot in the furnace for some time (up to 3 days) at a temperature of from 1350°C . to 1400°C . Lacking this treatment, the life of the pot in a modern gas-fired furnace will be very short. When, however, the working temperature in the pot does not rise much above 1200°C . the treatment may be dispensed with; but since softer and generally more corrosive batches are melted at such a temperature it would still be advisable.

The "vitrified" pot, when glazed or filled with glass, is subject to the solvent action of the alkalis in the glass batch. The solvent action tends to result in the formation of layer of sillimanite over the interior of the pot in contact with the glass. This layer gives a measure of protection from subsequent corrosive action. A pot which has not been fired to a high temperature before filling with batch tends to scale or become pitted much more readily, its life is shorter, and the quality of the glass may be inferior.

(250) **Setting the Pot.**—The pot, when in the pot arch, is usually placed upon bricks. When ready for transference to the furnace, which is already heated to the same temperature as the pot, the fronts of furnace and pot arch are pulled down. A strong carriage is wheeled under the pot, which is lifted and carried into the furnace and lowered into its desired position. Then the furnace front is quickly built up again.

As may be imagined, the operation of pot-setting entails a tremendous amount of hard labour under terrific heat on the part of the glass-workers. Bricks or blocks are removed from the furnace front with long irons, the process being arduous and rather lengthy. These, or new blocks, are again set up after the introduction of the pot by a string of men who, following one after another, dart across the front of the furnace and place a clayed block into position. Much time, labour, and energy may be saved by the use of a chain screen such as described in Chapter XV., whereby the furnace temperature is not sensibly lowered during pot-setting and there is less danger of cracking the pot.

* *Loc. cit.*

CHAPTER XXIV

FURNACES

Introductory.

(251) **General.**—Even though recent years have witnessed a great stimulus in the development of furnace plant designs in Great Britain, many manufacturers still rely on heating methods of most antiquated kinds. It will be our endeavour in dealing with the subject of glass melting furnaces to show, in as clear a manner as possible, the folly of retaining those of the old-fashioned "*direct-fired*" type, by a comparison with the more efficient gas-fired furnaces, which are likely for many years to come to hold sway in the glass industry. Oil-fired furnaces have their uses and are very advantageous in some cases, whilst there is a possibility of the use of powdered coal fuel, sprayed from burners in the same manner as oil, but neither of these forms of heating is in the near future likely to threaten the pre-eminence of producer gas firing.

A glass furnace may be defined as a piece of apparatus designed to give economically, either a high temperature, uniformly distributed over a hearth of large dimensions, or a temperature varying at will over different parts simultaneously. It will be shown later, when furnaces are described in detail, that direct-fired furnaces are very far from answering these requirements, whilst later types approximate much more to the ideal.

(252) **Types of Glass Furnaces.**—The furnaces at present used in the industry may be divided into the following classes:

(a) **Direct-Fired Furnaces.**—In these furnaces the firebox forms an integral part of the combustion chamber in which the glass is melted. All the air used for burning the fuel passes through the grate and the fuel bed itself.

(b) **Semi-Direct-Fired Furnaces.**—The fire-boxes are somewhat removed from the melting furnace itself, and the gases from the fuel pass directly from the fire-box into the combustion chamber through a narrowed entrance termed the "eye." Only part of the air used for burning the fuel passes through the grate; the rest, termed "secondary" air, passes first through flues surrounding the fire-box, and is so slightly "preheated" before mixing with the gases obtained from the fuel, at a point just before these reach the eye of the furnace.

(c) **Producer-Gas-Fired Furnaces.**—In this class of furnace heating is obtained by burning gas brought from a distinct apparatus, the pro-

(d) *Oil-Fired Furnaces*.—Oil, finely sprayed or “atomised” by admixture of air or steam under pressure, is burned in the combustion chamber by mixing with secondary air as in the case of producer gas. Oil-fired furnaces are generally provided with recuperators or regenerators.

Pot furnaces are those in which the glass is melted in pots or crucibles placed in the combustion chamber.

Our method of tabulation of the varying kinds of furnaces now may be given as follows:

<i>Pot Furnaces.</i>	<i>Tank Furnaces.</i>
Direct fired.	—
Semi-direct-fired.	Semi-direct-fired.
Producer gas fired with regeneration.	Producer gas fired with regeneration.
Oil "fired with "recuperation.	Oil "fired with "recuperation.
Oil "fired with "recuperation.	Oil "fired with "recuperation.

(254) **A Comparison of the Efficiency of the various Methods of Heating—Flame Temperature.**—In our discussion of fuel we have seen that the total heat which can be obtained from a certain quantity of any fuel is a fixed amount. Part of the heat so obtained is used in the furnace for melting the batch and fining the glass, part for maintaining it in a fluid condition for working, whilst the remainder must be regarded as waste heat, possibly capable of utilisation in some manner.

The total heat obtained from the fuel is employed, in the first place, in raising the temperature of the gaseous products of combustion, from which it is later given out to the glass, to the furnace walls, to the incoming gases, etc., or else carried away from the furnace as sensible heat of the gases themselves.

Since at first the *whole of the heat* is given to the gaseous products, the theoretical temperature to which these gases would be brought, when burned at constant pressure as in the glass furnace, would be quite fixed and definite, and this temperature is known as the *temperature of combustion* of the fuel. In active practice the *flame temperature* obtained is somewhat lower than the theoretical temperature of combustion, since combustion in a furnace is not instantaneous, nor is the whole of the heat produced by the combustion retained in the furnace.

Since the temperature of combustion is dependent upon the extent to which the residual gases can be heated by the fixed amount of heat supplied, this temperature will naturally depend upon the specific heats of the residual gases. If a gas possessed a fixed specific heat at all temperatures (s) and it was heated over a range from temperatures T_1 to T_2 , the heat absorbed, or the *thermal capacity* of the gas between T_1 and T_2 , would be $Q = s(T_2 - T_1)$. The specific heats of gases, however, are variable quantities and increase with increasing temperature. It has been found that the thermal temperature capacity for any gas (*i.e.*, the number of calories of heat absorbed) in heating from a temperature T_1 to a temperature T_2 is given by the formula:

$$Q = \frac{6.5(T_2 - T_1)}{1000} + \frac{b(T_2^2 - T_1^2)}{1000^2},$$

in which " b " is a constant, varying for different gases. Its values for the more common gases are given in Table XCV.

TABLE XCV.

" Gas."	Perfect Gases (O_2, N_2, H_2, CO).	Water Vapour (H_2O).	Carbon Dioxide (CO_2).	Methane (CH_4)
" b "	0.6	2.9	3.7	6.0

It will be seen that the greater the value of " b ," the more the heat that is required for raising the temperature of the gas over the interval. Conversely, if the heat supplied Q is fixed, the smaller will be the temperature increase $T_2 - T_1$, the greater " b " becomes.

The temperature of combustion of carbon in cold air (no excess) is $2040^\circ C$., whilst with a 25 per cent. excess of air it is $1650^\circ C$. Since in direct-fired furnaces it is practically impossible to secure complete combustion without a large excess of air, the temperature $1650^\circ C$. may be regarded as the extreme maximum combustion temperature, and the flame temperature will be considerably less. This shows the impossibility of obtaining really high temperatures by direct firing.

If the products of combustion contain carbon monoxide, a higher combustion temperature is possible. Thus, for instance, if the waste gases contain 5 per cent. of carbon monoxide a combustion temperature of $1930^\circ C$. may be obtained. Such a composition of the waste gases can only be secured by the regulation enjoyed by the use of gas-firing,

and, although in this case more coal will be consumed, we may attain appreciably higher temperatures than when direct firing is employed.

(255) **Regulation of the Temperature.**—In direct-fired furnaces little accurate regulation of combustion is possible. Indeed, conditions are so bad that frequently much of the combustion of the gases occurs when these have left the combustion chamber. Semi-direct-fired furnaces are somewhat better in this respect, but leave much to be desired. In gas-fired furnaces the means of regulation are so varied—*i.e.*, gas and air velocity, pressure and amount, chimney pull, etc.—that accurate regulation is quite feasible. In this respect the same recommendation may be given for oil-fired furnaces. In the latter types a further advantage is that variations of temperature may be made and maintained in different parts of the combustion chamber.

(256) **Utilisation of Waste Heat.**—One of the sources of loss of heat in all furnaces lies in the sensible heat carried away by the waste gases. If these pass away from the furnace at temperatures of 1200°C. to 1400°C. a very large amount of the heat of combustion is lost for melting purposes. If, however, some of this heat can be retained, it will result in a distinct saving in the amount of fuel required. This object is not usually attempted in direct and semi-direct-fired furnaces, but in gas-fired furnaces is secured by regeneration or recuperation. By these processes the waste gases are caused to give out much of their heat to the gases passing into the furnace for burning. In general, regenerators preheat both the combustible gas and secondary air, whilst recuperators preheat only the secondary air.

The first effect of preheating furnace gases is to increase furnace efficiency and reduce the amount of fuel required. For instance, in the case of a furnace in which the air and gas are regeneratively heated from temperatures of 200°C. and 500°C. respectively to a temperature of 1000°C. before entering the furnace, Travers* has calculated an increased efficiency of the fuel of 54 per cent.

A second important factor is the increase of flame temperature secured by this means. Now the temperature of combustion of hydrogen in cold air is 1970°C. , that of carbon has already been given as 2040°C. , of carbon monoxide is 2100°C. , and of theoretical water gas ($\text{CO} + \text{H}_2$) is 2030°C. Against these temperatures of combustion we wish to contrast that of a producer gas of the following composition by volume:

Carbon dioxide	5	per cent.
Carbon monoxide	20	..
Hydrogen	12	..
Methane	3	..
Water vapour	2	..
Nitrogen	58	..

When burnt in air, both gas and air being preheated to 1000°C. , the temperature of combustion is nearly 2200°C. This high temperature shows the practical value of preheating the air and gas.

As a further example we may take the combustion of Pittsburgh Natural Gas with the following composition by volume:

* *J. Soc. Glass Tech.*, 1921, 5, 179

Methane (CH_4)	67.0 per cent.
Hydrogen (H_2)	22.0 "
Ethylene (C_2H_4)	1.0 "
Ethane (C_2H_6)	5.0 "
Carbon monoxide (CO)	0.6 "
Carbon dioxide (CO_2)	0.6 "
Oxygen (O_2)	0.8 "
Nitrogen (N_2)	3.0 "

In Table XCVI. are given the temperatures of combustion of this gas under certain specified conditions.

Thus, whilst excess of air causes a reduction in the temperature of combustion, the reduction is less pronounced when the air is preheated. The higher the temperature of combustion the higher is the flame temperature also; other things being equal, a hot flame gives up more heat

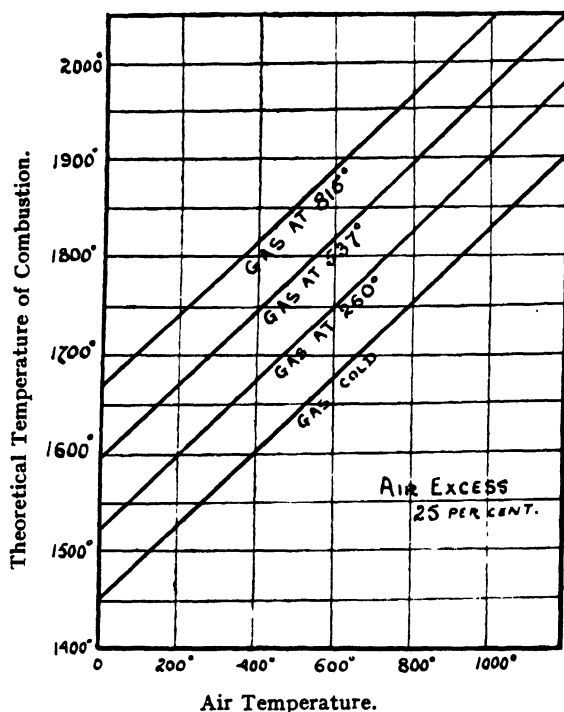


FIG. 107.—COMBUSTION TEMPERATURES OF RICH PRODUCER GAS.

to a furnace than a cooler flame, and hence the rate of heating is increased. Against this one must consider that the proportion of heat given up by the gases decreases very rapidly as the furnace temperature increases.

An interesting series of calculations has been made by Denk* in connection with the theoretical temperature of combustion of producer gases regeneratively preheated, and his results are expressed in graphic form in Figs. 107 and 108. In the first diagram (Fig. 107) are given

* *National Glass Budget*, 1919-20, 28, 1; 1919-20, 29, 1.

TABLE XCVI.—TEMPERATURES OF COMBUSTION OF NATURAL GAS.

<i>Temperature of Air.</i>	<i>Amount of Air.</i>	<i>Temperature of Combustion</i>
		<i>Degrees C.</i>
In cold air	No excess	1900
With air preheated to 1,000° C.	No excess	2415
In cold air	25 per cent. excess	1660
With air preheated to 1,000° C.	25 " "	2235

curves showing the combustion temperatures of a rich producer gas (30 per cent. carbon monoxide, 4 per cent. carbon dioxide) when cold or when preheated to temperatures of 260° C., 540° C., and 815° C., and burned with an air excess of 25 per cent., also preheated to various temperatures. Fig. 108 illustrates the effect on the combustion temperature of using various amounts of air in excess of the theoretical

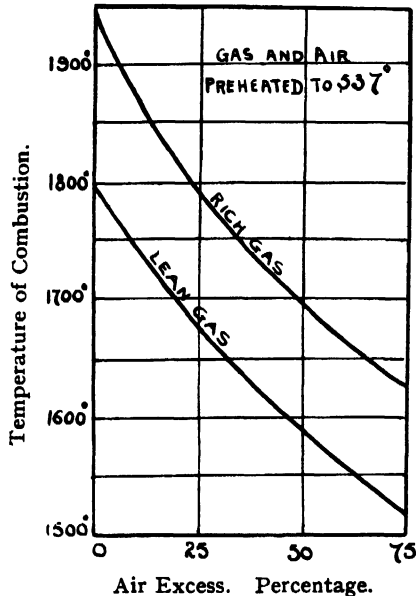


FIG. 108.—EFFECT OF EXCESS AIR ON COMBUSTION TEMPERATURE.

amount needed for combustion in the case of the previously considered rich producer gas and of a poor gas (20 per cent. carbon monoxide, 8 per cent. carbon dioxide), in the latter cases both air and gas being preheated to 540° C. Although it was found that the actual flame temperature was about 260° C. lower than the above calculated theoretical temperature of combustion, it was considered that, other conditions being equal, the above curves allowed of a fairly accurate estimate of the actual flame temperature being made.

CHAPTER XXV

DIRECT AND SEMI-DIRECT-FIRED FURNACES

(257) **"Old English" Pot Furnace.**—In order to trace the development of the glass furnace of modern type it will be interesting to note briefly some of the very early types of furnaces. The simplest form of furnace, and certainly the oldest, consisted of a chamber built of refractory material, in which was placed a pot or crucible to contain the batch, the pot being surrounded by a fire of wood or coal. In Fig. 109 is shown an old-fashioned, coal-fired pot furnace, used for the melting of flint glass,* and containing several pots. The fuel burns on the grate **A**, the flames from the burning fuel surround the pots, and the products of

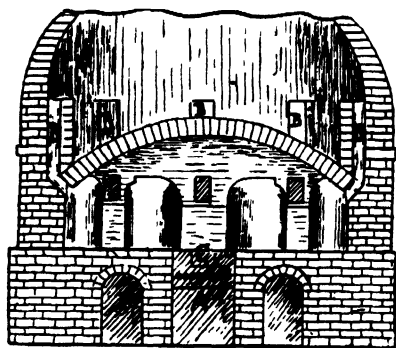


FIG. 109.—A "DIRECT-FIRED" POT FURNACE.

combustion pass out of the furnace chamber through small flues (**B**). They pass into the wide, outer conical chimney (not continued to its full height in the diagram) and finally into the atmosphere. The fire needs constant attention if a high working temperature is required, for the coal must burn at the greatest possible rate in order to attain a temperature of, say, 1300°C. to 1350°C. around the pots. Only a very small porportion of the total heat available in the fuel can be utilised in the furnace, since the flames pass into the flues at a temperature very little below that at which they enter the furnace chamber. As a result, the greater portion of the heat derived from the fuel passes into the

* J. W. COBB, *J. Soc. Glass Tech.*, 1917, 1, 223.

outer cone and is wasted. Various slight modifications in the arrangements of the flues have been tried in furnaces of this kind, with the view of utilising a little more of the heat available, but with no appreciable amount of success. Quite apart from heat losses, which render such a furnace as this most inefficient, the fact that the fire is so close to the furnace chamber results in the light ash being carried into the chamber with deleterious effects upon the walls, pots, and colour of the glass. Inattention to the fires, resulting in varying temperatures in the furnace, may cause cracking of the pots, and then, unless the glass is quickly ladled out, it runs over the "siege," as the bottom of the furnace is called, and over the fire and firebars. This at once hinders the working of the furnace and may damage other pots.

A furnace of the type just described will melt glass, not of the most resistant quality, at the rate of one ton of glass per three to seven tons of coal, a fact quite sufficient to condemn any furnace at the present time.

(258) **The Frisbie Feed.**—In some direct-fired pot furnaces an attempt is made to improve the firing arrangements by adopting a mechanical device known as the Frisbie feed. By use of this feed, which is fitted underneath the bars of the furnace, fuel is fed upwards into the furnace box instead of downwards, as in the furnace already described. As fresh fuel is pushed up in small charges by the mechanism into the fire, all the products of combustion must necessarily pass upwards through the hot fire. The result is that a semi-Siemens producer effect is obtained, and the fuel is largely gasified and partly burned on the grate. The gases pass up into the eye and are burned in the furnace, finally passing through the small flues into the cone. Better combustion and also a higher temperature are obtained by this means, whilst the fuel consumption is slightly reduced. The furnace remains inefficient, however, for the reasons given in the next section.

(259) **The Efficiency of Direct-Fired Furnaces.**—The thermal efficiency of the direct-fired type of furnace is low because (1) a large excess of air, from two to three times the theoretical amount, must be used to obtain combustion. (2) The air supply cannot be readily regulated and the furnace temperature fluctuates, rising occasionally as the air supply approaches the exact quantity required to maintain complete combustion, but falling if the air supply is either insufficient due to clinkering of the fire, or in excess due to a shallow fuel bed or holes in the fire. (3) All systems of preheating pipes so far tried have proved quite useless. (4) Since the gases pass quickly through the furnace and the flame temperature is low, the drop in temperature between entry and exit is only slight, therefore only a small fraction of the available heat in the coal is capable of being utilised in the furnace.

This type of furnace may serve its purpose where (1) fuel is abundant, cheap, and of the long-flame variety; (2) the glass produced is of a high-class (table or decorative) nature; and (3) a cheaply and simply constructed furnace is desired.

a positive pressure, that is, a pressure greater than atmospheric, in which case air is prevented from entering the furnace through the secondary air ducts and combustion is incomplete.*

The Boetius furnace has had considerable vogue in Germany, Belgium, and Britain, but, like the direct-fired furnace, is likely to disappear from active use.

Semi-Gas-Fired Day Tanks.—"Day" tanks are those in which the glass is melted overnight and worked out during the following day.

If one may imagine the Boetius furnace cut into two parts, the portions separated, and a tank placed between them, an arrangement is obtained such as is shown in Fig. 112.

The furnace is operated in a manner very similar to that of the pot furnace. Secondary air flues lead from below the grate, pass around the fire-box, and open by narrow ports into the communicating flue between fire-box and tank. The grates are arched over, thus giving a

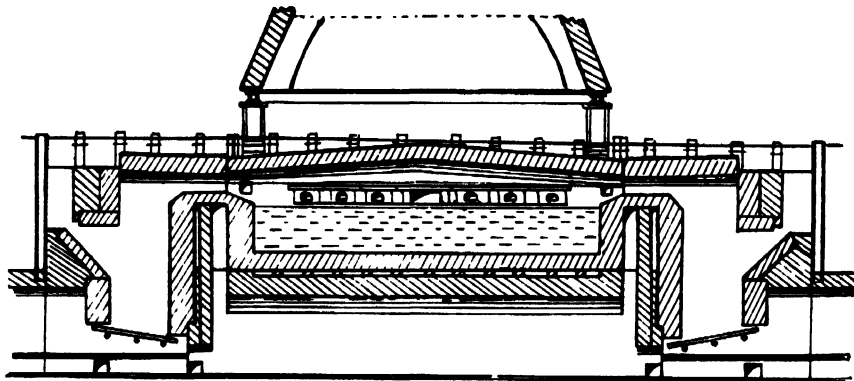


FIG. 112.—A SEMI-GAS-FIRED DAY TANK.

sort of gas-holder over the fires, from which flues lead directly to the ports. Exit flues lead from the centre of the walls of the tank and into the air as in the pot furnace.

(261) **The Travers and Clark Furnace.**—Furnaces of the Boetius type have been largely increased in efficiency by a patented device of Travers and Clark. A great fault of the ordinary Boetius furnace is that there is not generally a sufficiently low pressure at the secondary air ports to allow of sufficient air to enter and burn the gas. Indeed, it has been found that these ports were sometimes even under a positive pressure and gas from the fires was being forced down and burnt in the flues. To remedy this defect the Travers and Clark furnace is provided with a blower to drive the secondary air through the flues and into the furnace. It is claimed that by this device a lower temperature may be maintained in the fuel-bed without decrease of temperature in the furnace.

* See also TRAVERS, J. *Soc. Glass Tech.*, 1920, 4, 205.

CHAPTER XXVI

GAS-FIRED FURNACES—REGENERATIVE

(262) **Regenerative Preheating.**—Gas-fired furnaces date back to the patents granted to F. and W. Siemens in 1856 and 1861. The Siemens regenerative furnace was first tried successfully in 1867 at the plate-glass works in St. Gobain, but was not adopted generally by the plate-glass industry until 1876, after the tank furnace had given good results. Before describing furnaces of this type we shall first consider the principles underlying the system of regenerative preheating of furnace gases.

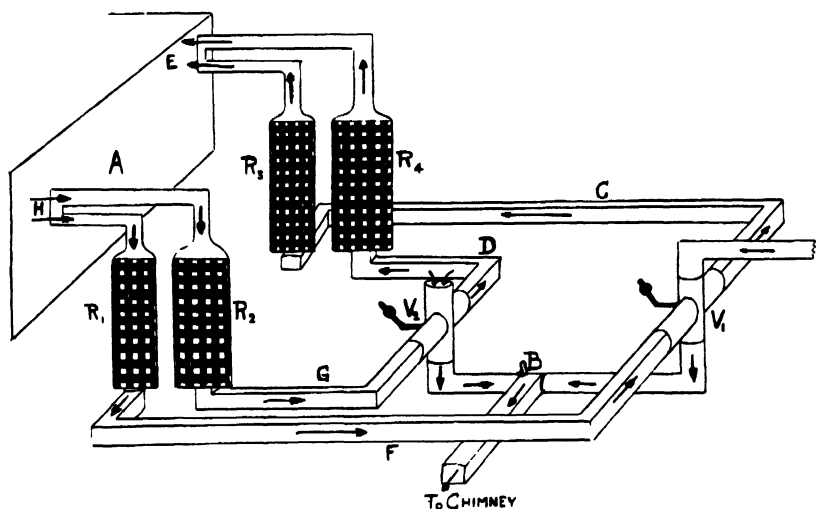


FIG. 113.—THE REGENERATIVE PREHEATING SYSTEM. (AFTER "DIE GLASINDUSTRIE IN JENA.")

Fig. 113 illustrates, diagrammatically, the details of the regenerative system. The products of combustion issuing from the furnace (A) pass through two chambers (R_1 , R_2) containing brick checker work. From thence they travel along flues to reversal valves (V_1 , V_2), through the valves to meet in another flue (B) and pass finally to the chimney. Meanwhile gas from the producer is entering the valve (V_1) and passing along a flue (C) into a regenerator (R_3) and thence to the furnace. Similarly, air enters the second valve (V_2), induced thereto by the chimney draught, passes along a flue (D), through a regenerator (R_4), to meet the gas at

the port (**E**) in the furnace. It will be obvious that the chambers **R**₁ and **R**₂ will be increasing in temperature during this process, whilst **R**₃ and **R**₄ will be cooling, the heat lost by the latter pair being conveyed to the furnace by the ingoing gas and air. After this has been going on for a certain time (usually thirty minutes) the direction of the gas and air currents is reversed. Accordingly, the gas entering valve **V**₁ now passes along the flue **F** to the chamber **R**₁ and thence to the furnace, whilst the air entering valve **V**₂ passes along flue **G**, through regenerator **R**₂, to meet the gas at the furnace in the port **H**. The products of combustion, issuing at **E**, pass through the chambers **R**₁ and **R**₂, along flues **C** and **D** to valves **V**₁ and **V**₂, again meeting at **B** and passing up the chimney.

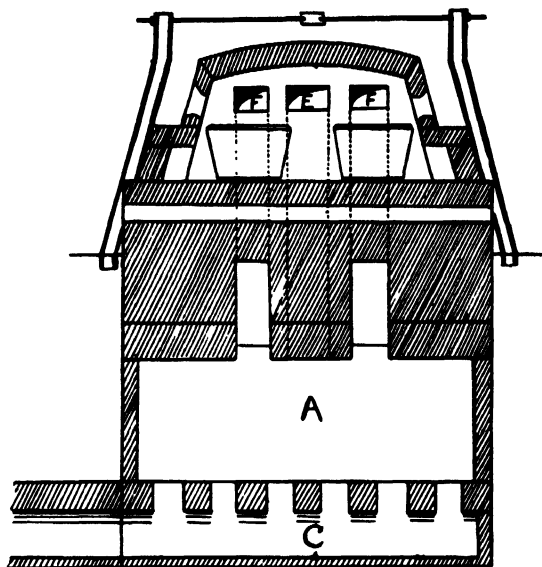


FIG. 114.—A SIEMENS REGENERATIVE GAS-FIRED POT FURNACE (CROSS-SECTION).

(263) **Pot Furnaces—Regenerative.**—Figures 114 and 115 show a Siemens regenerative, gas-fired pot furnace with ports above the pots. The two air regenerators (**AA**) are placed in the centre below the furnace proper, flanked by the gas regenerators (**BB**). Air and gas pass from the reversal valves into the regenerators by the flues **CC** and **DD** respectively. The gas passes into the furnace by ports **E** and air by ports **F**, the flames moving alternately from left to right and right to left as the currents are reversed. The furnace will give high temperatures, but it has the disadvantage that the temperature is not uniform, being hotter at one end than the other, the hot end being that nearest to ports at which the flame enters. Each end is therefore alternately hot and cold.

(264) **The "Slit" Büttel Furnace.**—Another regenerative gas-fired pot furnace, of the "Büttel" type, is illustrated in Figs. 116 and 117. In this furnace gas and air enter at the siege level, and the products

of combustion are drawn off similarly. Whilst gas and air from the regenerators **A** and **B** pass through ports **CC** on the left-hand side of the

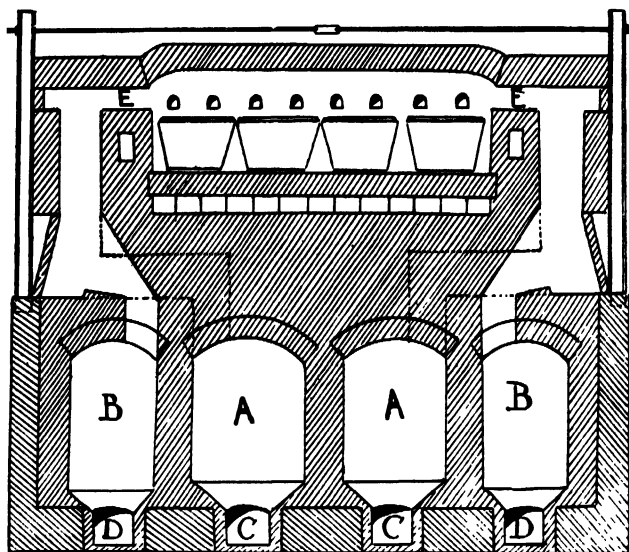


FIG. 115.—A SIEMENS REGENERATIVE GAS-FIRED POT FURNACE (LONGITUDINAL SECTION).

furnace the waste products pass down the ports **DD** on the right-hand side, through the other regenerator, and to the valves and chimney. On reversal of the currents **CC** become exit ports and **DD** entry ports.

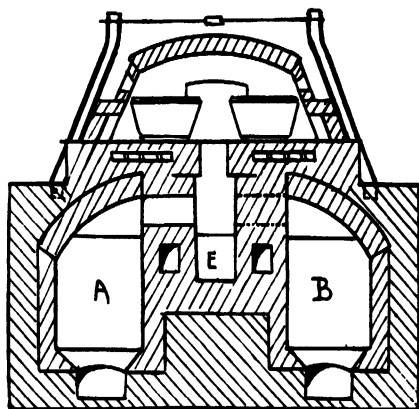


FIG. 116.—THE BÜTTGEN FURNACE (CROSS-SECTION).

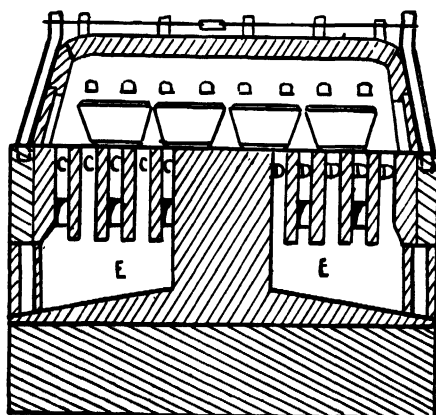


FIG. 117.—THE BÜTTGEN FURNACE (LONGITUDINAL SECTION).

This furnace also burns one-sidedly, but it possesses an advantage in that the exit of gas and air from the regenerators lies deep below the

siege and the air and gas pass side by side up the slit-like ports. In the case of pot breakage the glass runs down the slits and into pockets **E**, from which it can be removed.

MODERN REGENERATIVE POT FURNACES.

(265) **The "Harvey-Siemens" Furnaces.**—The Harvey-Siemens patent regenerative gas furnace is an improved form of the ordinary Siemens furnace which has been extensively applied for melting glass and for other purposes. In the older Siemens furnace, already mentioned, the gas-producers are built some distance away from the furnace, which, as shown in Fig. 115, has four regenerators. With the "Harvey-Siemens" furnace the gas-producers are either incorporated with the furnace or else are located very close to it. Only two regenerators are used, these being for air alone, whilst the producer gas is used "hot."

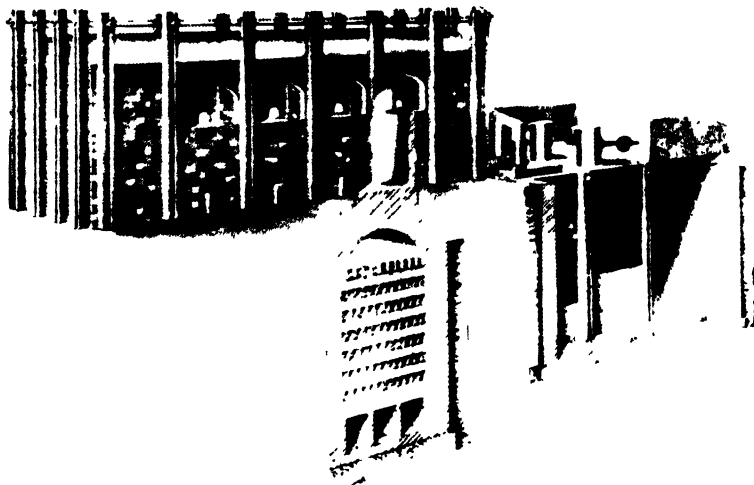


FIG. 118.—THE "HARVEY-SIEMENS" REGENERATIVE POT FURNACE.

(By courtesy of the E. W. Harvey Gas Furnace Co., Ltd., London.)

The gas-producers of the "Harvey-Siemens" furnaces are of the water-bottom type (*i.e.*, without grates) of a special design, being extremely simple and ensuring an absolutely regular production of gas. In order to economise manual labour, the gas-producers may be charged automatically in a very simple manner by the installation of a feeder of a new design, worked by a small motor or steam-engine.

The gas valves are specially water-cooled in such a way that only a small quantity of water is required. These valves are very durable and will last about twenty years, or at least as long as a steam boiler.

The advantages secured by the "Harvey-Siemens" furnace, as compared with the older Siemens furnace, are briefly as follows:

1. The furnace, with its gas-producers, occupies much less ground space, usually about one-half.
2. There is a large saving in the cost of construction, usually from 30 per cent. to 50 per cent.
3. The furnace is simpler in construction and easier to work and regulate.
4. There is a considerable saving in the frequency and cost of repairs, owing to the simpler construction and the smaller number of parts.

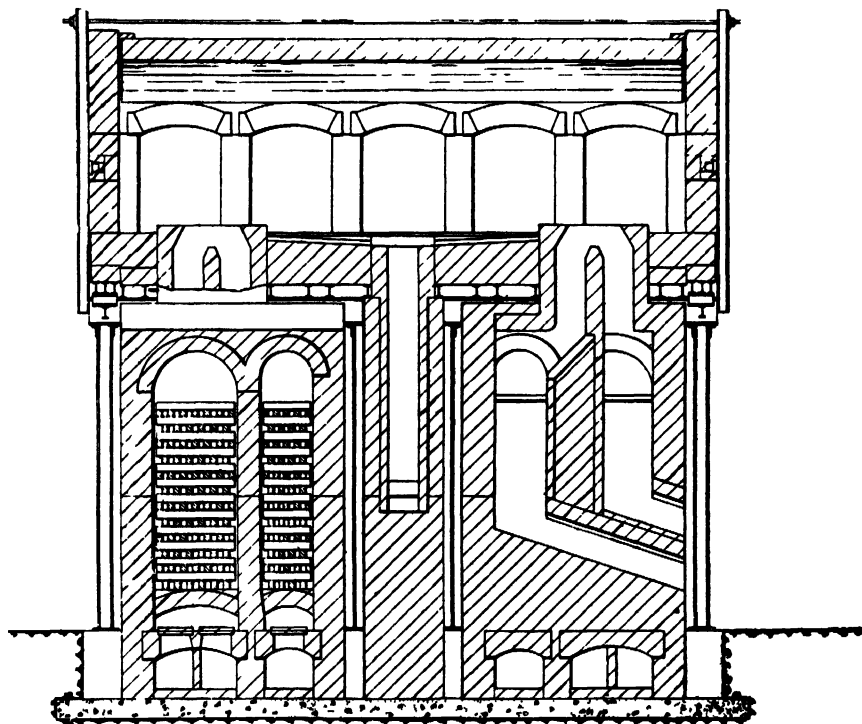


FIG. 119.—A "SIMON-CARVES" REGENERATIVE POT FURNACE.
(By courtesy of Messrs. Simon-Carves, Ltd., Manchester.)

5. There is an important economy of fuel, usually from 25 to 30 per cent., the coal used at some works having been brought as low as 16 cwt. per ton of finished bottles.

The "Harvey-Siemens" furnaces are designed for melting glass in continuous or intermittent tanks, open or closed pots, and "skittle" pots. Here we are concerned only with the pot furnaces. Fig. 118 shows a pot furnace holding eight large covered pots. The working holes are on each side of the furnace, which is heated by a reversible flame passing from end to end.

(266) **"Simon-Carves" Furnaces.**—A sectional view of a standard ten-pot regenerative furnace for large pots, designed by Messrs. Simon-Carves, Ltd., is shown in Fig. 119. The main feature of this furnace is

that the regenerators are separate structures and do not support any of the weight of the furnace. The siege and combustion chamber of the

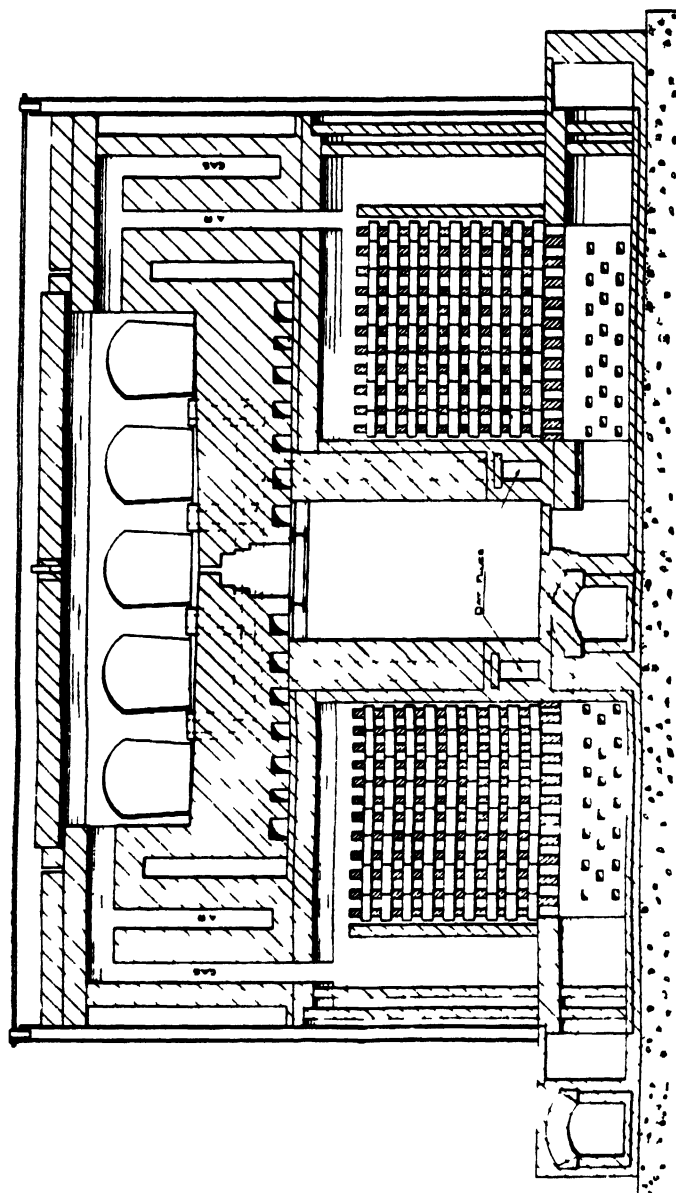


FIG 120 —A "SIMON-CARVES" DAY POT FURNACE
(By courtesy of Messrs Simon-Carves Ltd., Manchester)

furnace are supported upon a gantry constructed of steel joists and columns and spanning over the tops of the regenerators. The gas ports from the regenerators are provided with dust chambers and cleaning-

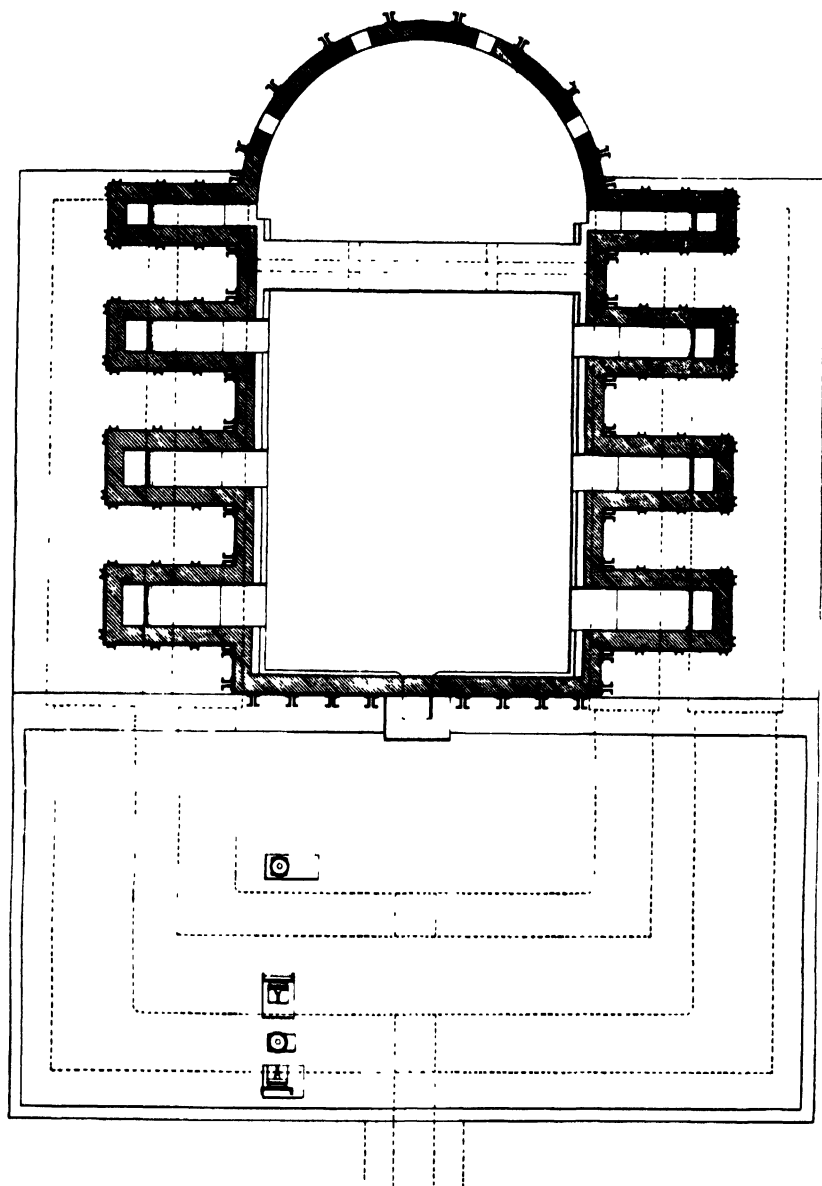


FIG. 121.—THE OLDER SIEMENS REGENERATIVE GAS-FIRED TANK FURNACE (PLAN).
(This and succeeding illustrations up to, and including, Fig. 128 are reproduced by courtesy of the E. W. Harvey Gas Furnace Co., Ltd., London.)

out passages at the bottom of the furnace, and in the centre a glass-pocket is provided in case a pot of glass breaks. The designers claim that with this furnace it is possible to plain a 35 cwt. pot of glass in 19 hours.

In Fig. 120 is shown a ten-pot furnace of the Bohemian type for

open pots. The pots are only of 7 cwt. capacity, and melting is done during the night-time and blowing during the day only. This may therefore be described as a "day-pot furnace," and was built by Messrs. Simon-Carves, Ltd.

(267) **Tank Furnaces—Regenerative.**—According to Schipmann,* day tanks came into operation as a result of increased pot breakage caused by the introduction of gas-firing in furnaces.† He states that in a large Rhenish factory working a gas-fired regenerative furnace, the use of a considerably higher temperature resulted in all the pots in the furnace breaking. The glass spread over the sieve, pieces of broken pots floated to the surface and were removed. The glass was well "bubbled," batch was added to give the required working depth and the first "day-tank" so obtained.

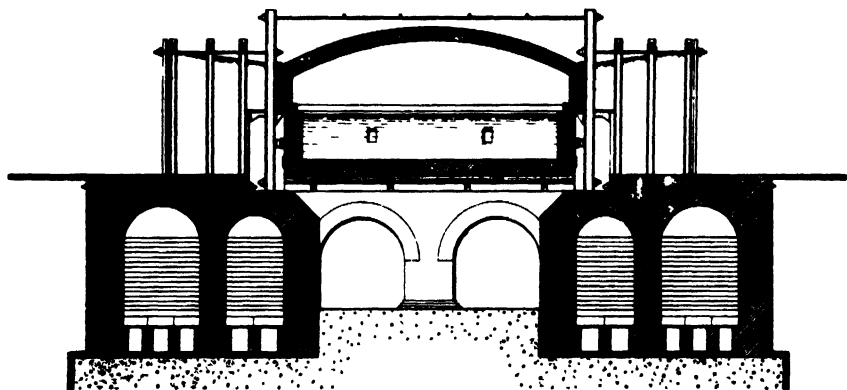


FIG. 122.—THE OLDER SIEMENS REGENERATIVE GAS-FIRED TANK FURNACE (CROSS-SECTION).

At the present time, day tanks are quite common in America. They are used for special purposes, generally where the nature of the glass required, or the quantity, is not such as to warrant the melting of it in a large continuous tank.

(268) **Continuous Tanks.**—Tank furnaces have a melting and a working zone. The end at which the raw material is introduced is usually straight and at right angles to the side walls. The working end of the tank is usually semicircular. The two zones may be separated by a "bridge" built from side to side of the tank, or left unseparated. If a bridge is used it has a hole (or holes) below the level of the glass, known as the "dog-hole," which permits of the passage of glass from the melting to the working end. The filling on of the batch takes place either through a door at the melting end or via a "dog-house," a box-shaped projection of the melting chamber which is filled with batch (see Fig. 56), the batch being pushed at intervals into the furnace through

* *Aus der Praxis eines Glashüttenfachmannes*, part ii., p. 9.

† It may be noted here, as Schipmann pointed out, that these pot troubles, occasioned by the higher temperatures of the gas-fired furnaces, were eventually solved.

a hole below the level of the raw material in the dog-house. Filling in by this method does not permit an entry of cold air into the furnace through the filling hole, the batch is warm or hot when filled in, and the furnace temperature is more easily kept constant.

Two distinct methods of firing these furnaces are used. In one the gas and air enter by a port or ports in the melting end of the furnace, sweep along its length, and then return to pass away down ports along-side the entry ports. By the second method gas and air enter at a series of ports along one side wall of the melting section of the furnace and

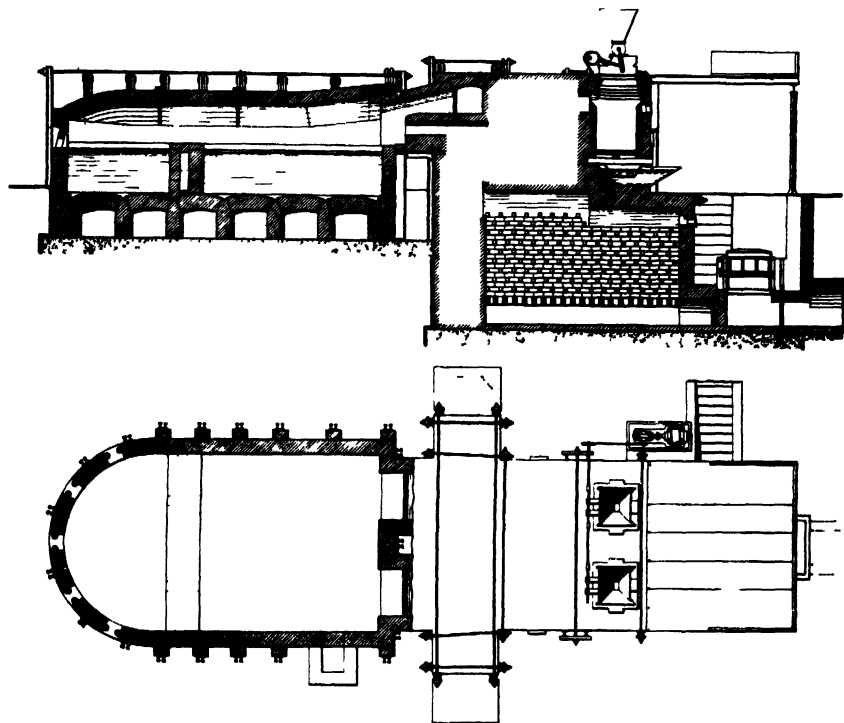


FIG 123.—THE "HARVEY-SIEMENS" REGENERATIVE TANK FURNACE (HORSE SHOE FLAME).

pass away down corresponding ports in the opposite wall. When reversal takes place, in both cases the original entry ports become exit ports and *vice-versa*. Furnaces of both types will be described.

The older Siemens regenerative gas-fired tank is illustrated in Figs. 121 and 122, and is fired in a manner similar to the pot furnace already described. It has gas and air regenerators, and is served by an independent battery of gas-producers.

The "Harvey-Siemens" patent regenerative furnace (Fig. 123), with gas-producers combined, has a horseshoe flame. The flame enters at one port, the velocity of the gases and their rapid expansion during com-

bustion carry the flame to the opposite end of the tank. The chimney draught operating through the other port draws the gases out of the furnace, the current of gases therefore taking, more or less, the shape of a horse-shoe.

The advantages which were claimed for the horseshoe flame type of furnace by Siemens were as follows:

(a) A longer flame (40 to 50 feet) is obtained than is the case with the old cross-flame type (20 to 25 feet), and accordingly the products of combustion remain longer in the hearth and give a better heating effect.

(b) The side walls of the tank are easy of repair, and the crown is usually supported, not by the walls, but by a separate iron framework.

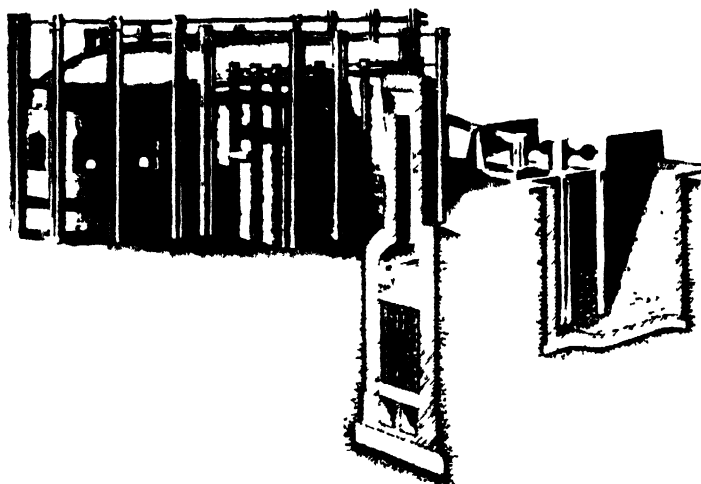


FIG. 124.—THE "HARVEY-SIEMENS" REGENERATIVE GAS-FIRED TANK FURNACE (CROSS-FLAME).

(c) The space required for erection is less and the cost of building is also less. Horseshoe tanks are usually not so broad as those of the cross-flame type of similar productivity.

(d) The workers are not usually subjected to the influence of radiant heat, since they do not work against gas, air and waste gas flues.

It is essential in this type of furnace that the flame shall be projected with sufficient force to carry it to the working end of the furnace, and that it shall not be drawn back to the exit port too quickly by the draught. Equally essential is the necessity for avoiding a flame of too great a length, which would burn in the working end of the tank and inconvenience the workmen. Ports in this type of furnace must be exceptionally refractory and carefully and accurately constructed, since the flames and dusty batch material rapidly corrode the ports they should be so built that repair or replacement is simple.

Fig. 124 illustrates a "Harvey-Siemens" furnace of the type just

described, but with a cross-flame instead of the horseshoe flame. Several gas and air ports are arranged on each side of the tank, and by suitable dampers the amount of flame entering the furnace through each of these

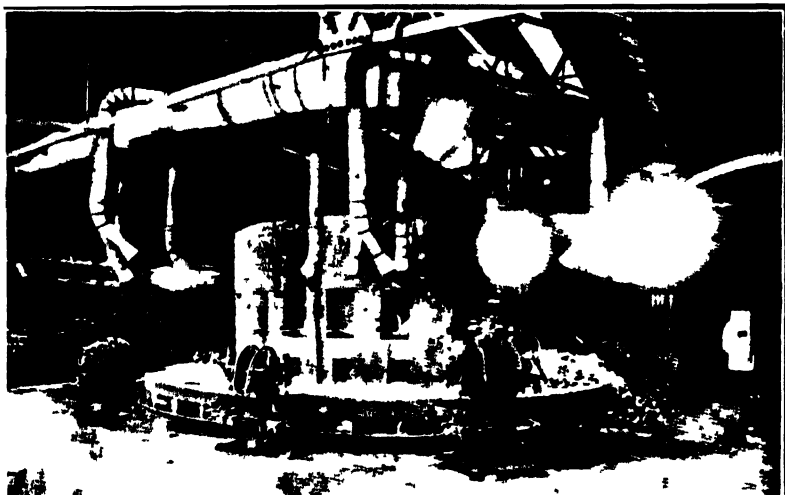


FIG. 125.—A "HARVEY-SIEMENS" FURNACE (HORSE-SHOE FLAME) FOR HAND-FED BOTTLE MACHINES

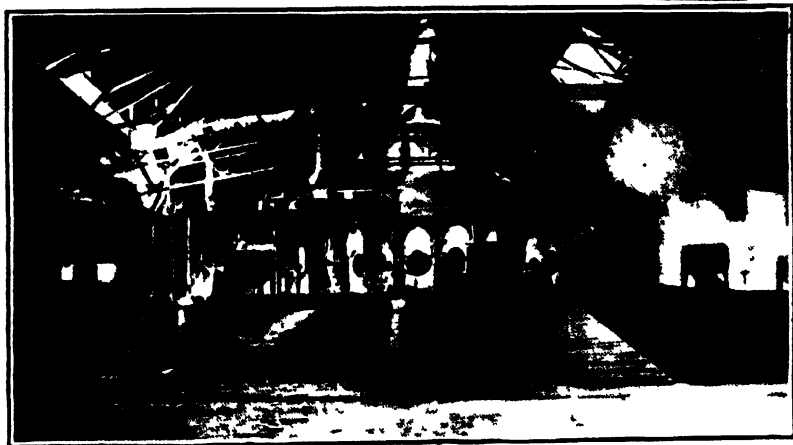


FIG 126.—A "HARVEY-SIEMENS" FURNACE (CROSS FLAME) SHOWING SWINGING PITS FOR HAND-MADE WINDOW GLASS CYLINDERS

ports can be properly regulated, so that the heat in different parts of the tank is under perfect control. Where a single-ended tank (as shown) of large capacity has been required, and a cool gathering end for hand-

made bottles, this furnace has given excellent results. A tank furnace of the horseshoe type for use with hand-fed bottle machines is shown

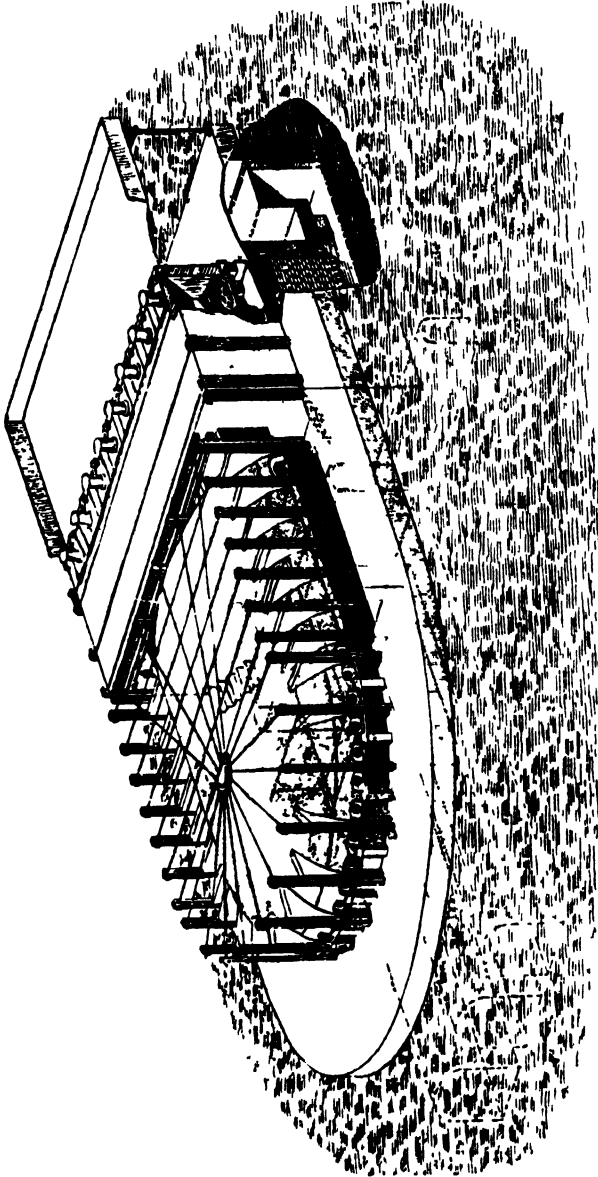


FIG. 127.—A "HARVEY-SIEMENS" FURNACE WITH TWENTY "HOLES" IN A SINGLE WORKING END.

in Fig. 125, whilst Fig. 126 shows the gathering and blowing holes at the end of a similar cross-flame furnace, and the swinging pits for hand-made window-glass cylinders.

A "Harvey-Siemens" furnace, with a single gathering end carrying 20 holes, heated by the horseshoe flame, is shown in Fig. 127. In this furnace the batch is filled on at the end opposite to the working end.

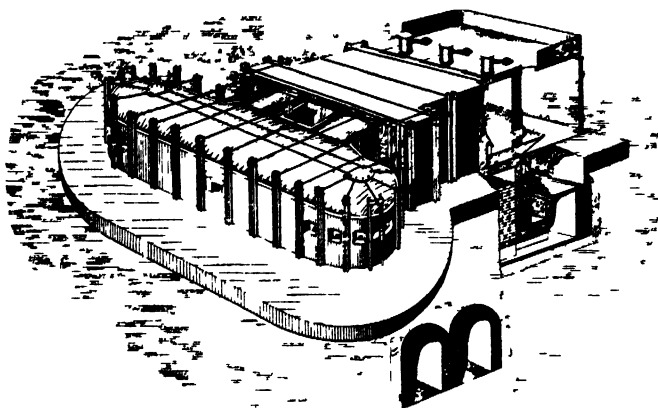


FIG. 128 —A "HARVEY-SIEMENS" FURNACE WITH TWO WORKING ENDS

Another horseshoe flame furnace with two ends for working is illustrated in Fig. 128. This tank is heated by a horseshoe flame in the centre part of the tank, and the batch is fed in on the opposite side of the tank.

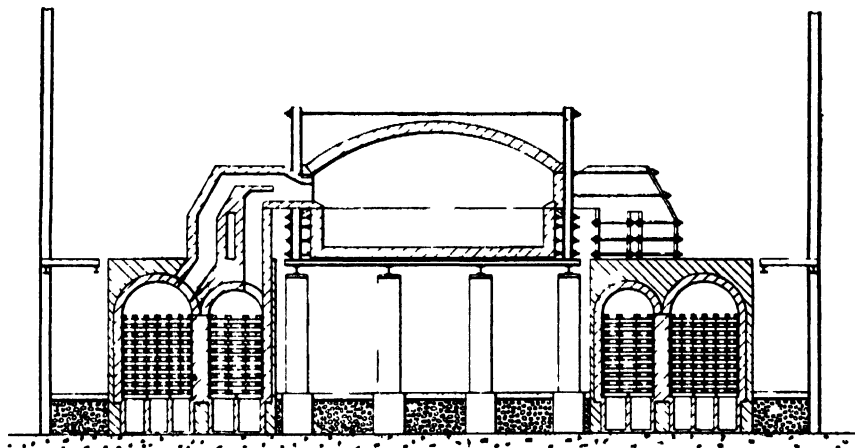


FIG. 129 —A "SIMON-CARVES" REGENERATIVE TANK FURNACE (CROSS-SECTION)

(By courtesy of Messrs Simon-Carves, Ltd, Manchester.)

A cross-section of a regenerative tank furnace, built by Messrs. Simon-Carves, Ltd., is illustrated in Fig. 129. In this case the tank is separately supported and does not rest in any way upon the regenerators (see pot

furnace, p. 339). The tank is a block structure, 12 inches thick throughout, the bottom resting upon a grillage of steel joists and flat bars, and the crown arch supported from heel plates.

(269) **Regenerative Furnaces, General Principles of Design.**—We now come to the individual consideration of essential parts of regenerative furnaces, and in this respect we must consider the reversal valves, regenerating chambers, flues, etc., as essential portions of the furnace itself.

(270) **The Relative Positions of Producers and Furnaces.**—The bottom of the fuel-bed should always be placed as far as is practicable below the furnace ports, particularly where ordinary open producers are in use. Owing to the constant opening of working holes in the furnace the chimney may have little direct effect upon the producer, and accordingly a head of pressure from the producer to the furnace must be maintained in order to force the gas into the furnace with the required velocity. The gas distributing system should therefore be as short as possible. The gas mains must be large enough to avoid obstruction to the passage of the gas, but not excessively so, since that would retard the velocity of the gas. Insulation of the gas mains is advantageous, since it prevents too great a fall in the temperature of the gas, which is accompanied by a condensation of tar vapour. The loss of tar vapour means a loss in heating efficiency, and the deposited liquid tar causes trouble with reversal valves.

(271) **Reversal Valves.**—These valves are used to direct to one side or the other the products of combustion and the gases required for the firing of the furnace, and they form the division line between the checker-chambers and the producer on the one hand and the checker-chambers and the chimney on the other.

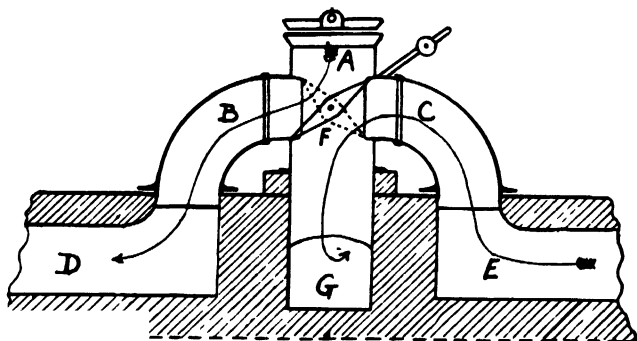


FIG. 130.—A SIMPLE AIR REVERSAL VALVE.

It is essential in the operation of a gas-fired regenerative furnace that the reversing valve shall operate rapidly and easily and be perfectly gas-tight. A simple type of air reversal valve is shown in Fig. 130. It consists of a cylinder (A) with cast-iron elbows (B and C) connecting with the flues D and E. Between the elbows inside the cylinder A is the valve F. When the valve is in the position shown in Fig. 130,

secondary air passes in at the top of the cylinder **A** through the elbow **B** and along the flue **D** to the furnace. The products of combustion from the furnace pass along flue **E** through elbow **C** and into the chimney **G**. When the valve is reversed into the position indicated by the dotted lines, the air passes by **A**, **C**, and **E** to the furnace, whilst the products of combustion pass from **D** through **B** to the chimney flue **G** as before.

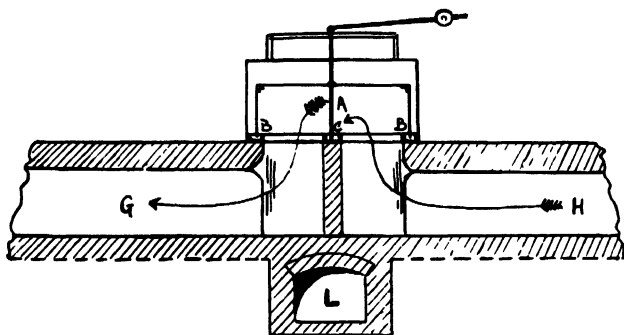


FIG. 131.—A GAS REVERSAL VALVE (SECTION).

A gas reversal valve is illustrated in Figs. 131 and 132. This consists of a cylindrical, sheet-iron drum with a diametrical dividing plate (**A**), which rests in a water-containing ring (**BB**) with cross-channels (**CC** and **C'C'**). When the dividing plate is set in the position **CC** as shown in Fig. 132, the gas from the gas-producer enters the drum by flue **D** and passes along to the furnace by flue **G**, whilst the products of combustion

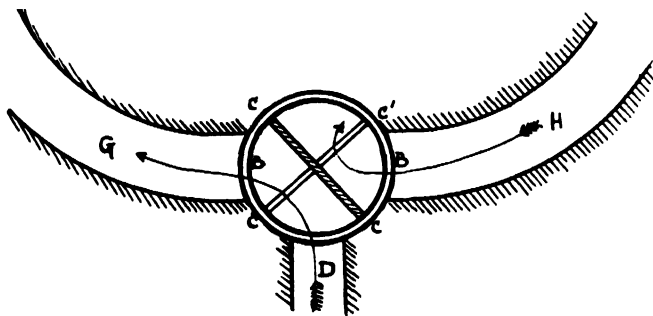


FIG. 132.—A GAS REVERSAL VALVE (PLAN).

from the furnace pass by flue **H** into the chimney flue **L**. On reversal, the dividing wall reaches position **C'C'** and the producer gas passes to the furnace by **H** and waste products by **G** to the chimney flue **L**.

It is essential, particularly with the gas-reversal valve, to avoid distortion due to heat, since distortion will result in leakage. The only valves which remain tight at all temperatures are water-seal valves, providing the level of the seal is kept horizontal. The one grave defect

of these is the vapourisation of water from the seal, the water-vapour being carried along by the gas.

A water-cooled valve constructed by the W. R. Miller Company,* of Pittsburg, Pa., is illustrated in Fig. 133. The valve plate, wall plates, and bottom seal are made of welded steel for a water-cooling system, although the bottom seal, if preferred, may consist of a casting with air circulation. Large valves are operated by electric motors and small ones by hand-operated rigging.

A gas reversing valve (which can also be used for air reversal) of the water-sealed type is the Wellman Gas Reversing Valve. The general design and construction of the Wellman valve are clearly shown in the phantom view in Fig. 134. It will be seen to consist of an outer casing, a base with three ports, a hood to connect two ports, and the operating mechanism.

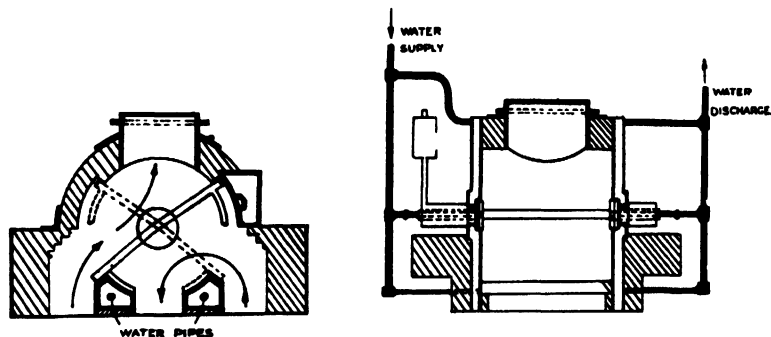


FIG. 133.—THE W. R. MILLER WATER-SEALED GAS REVERSAL VALVE.

The centre port is connected to the chimney. Waste gases from the furnace flow from whichever outside port the hood is covering to the chimney port. This leaves a clear passage for the fuel gas or the air entering the casing through the mushroom valve at the top to pass through the third port to the furnace or regenerator. Reversal of the flow of gas or air is accomplished by moving the hood to a position over the centre port and the one previously uncovered. The base of the valve is a cast-iron rectangular pan, with three walled openings or ports. The hood, which covers the centre and one end port, is semi-elliptical in form, and consists of a heavy steel or mild steel casing having a cross bar tying the sidewalls together as well as pockets to engage the supporting levers. This construction does not require brick lining.

The base pan holds a quantity of water, so that when the hood is over the ports, a water seal is formed to prevent the escape of gas. The base pan has a tapped hole at each end for a water pipe. There is a perforated strainer at the intake end and a dam plate at the other end to hold the water at such a level as to allow the hood to extend three inches into the water forming the seal. The outer casing is made of steel plate and should be lined with fire brick, if producer gas is used. It has cast-iron door frames and a door at each end through which the

* *The Glass Industry*, 1922, 3, 102.

hood may be removed or inserted. Each door has a small peep-hole with a swinging cover, which enables inspection at any time. On the top of the casing is a cast-iron neck which connects either with the fuel gas flue or the air intake, depending upon the purpose for which the valve is used.

The hood is moved by a series of levers and coupling shafts which extend through the water under the casing and into sockets on the hood. The shafts move on chilled iron bearings. At each side of the valve is a counterweight attached to an arm and sector over which passes a chain connecting with the supports of the hood. The form of this sector is such that the counterweights balance the weight of the hood at any position.

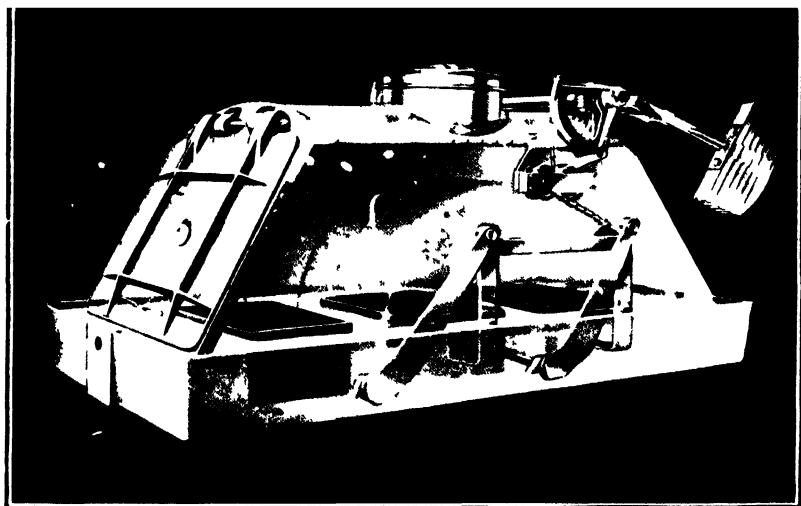


FIG 134.—THE WELLMAN GAS REVERSAL VALVE.

(By courtesy of the Wellman, Smith, Owen Corporation, Ltd, London.)

This new valve is similar in principle to the well-known **Forter Valve**, which was manufactured exclusively by the Wellman-Seaver-Morgan Company in America.

(272) **Regenerating Chambers.**—The function of these chambers is to store up heat imparted by hot waste gases from the furnace for a period, and then, when the reversal has taken place, to give out the heat so stored by the brickwork to currents of colder producer gas and air, by which the heat is conveyed once more to the furnace. It is obvious that the temperatures of gas and air will be increased rather more when first admitted into the chambers than at a time immediately prior to reversal. The shorter the period between reversals the more regular the furnace temperature, and, up to a certain limit, the higher is this temperature also. The difference in temperature between the

preheated air and gas entering the furnace and that of the waste gases leaving it is about 350°C .

Regenerators should be neither too large nor too small. Large regenerators cost more to build, occupy more space, and radiation of heat from the outside walls becomes high. As the volume of the gas chambers increases, the loss of heat due to the gas filling them at the time of reversal is also increased, and the temperature of the waste products may be so decreased as to impair the chimney efficiency. Since the gas usually enters the regenerators at a considerably higher temperature than the air, and is considerably less in volume, the gas regenerator is always smaller than the air regenerator,* the sizes being so regulated that the velocity of both gas and air on entering the furnace is the same.

The chambers should be grouped in one block approaching a cubical form in order to reduce the loss by radiation. The longer axis may be vertical or horizontal, but, generally speaking, the vertical type has the better thermal efficiency. The walls should be at least 13.5 inches, and, better, 18 to 22.5 inches in thickness. Dividing walls should be of the same thickness in order to avoid, as far as possible, leakage from one chamber to another.

Bricks or blocks used in regenerators should readily absorb and give out heat, and all the refractory materials used should be as resistant as possible to the fluxing action of the glass-batch ingredients which may be drawn or blown into them.

The ratio of the width of the open channels to that of the dividing walls in the regenerators should be in relation to the specific heats of the gases and of the refractory materials used. The open spaces should be larger for the gas than for the air chambers, in which the ratio may be made equal to unity. Various recommendations have been made regarding the relative volumes of chambers and checker-work, but it is possible to calculate the correct relation for any given conditions. Siemens recommended a total surface of 51 square metres of checker-work per 1,000 kilograms of coal consumed in 24 hours. Toldt gave a volume of 6 cubic metres and a weight of 2,850 kilograms per cubic metre of gas or air (at 0°C . and 760 mm. pressure) for each 100°C . rise in temperature in the regenerator. His value is somewhat low. Standard American steel practice (where higher temperatures are required than in the glass industry) allows three times the capacity stipulated by Toldt. Grüner suggested that the weight of checker-work should be 230 kilograms per kilogram of coal burned between reversals.

The flue passing beneath the checker-work should be of sufficiently large cross-section to ensure that the gaseous currents will be forced to distribute themselves throughout the whole volume of the chamber. An arrangement as shown in Fig. 135 results in portions of the checker-work, as at **A** and **B**, being wasted. An ideal arrangement is shown in Fig. 136. In any case, sharp corners or bends, too close checker-work, or choked chambers result in inefficiency due to diminished draught from the "chimney-pull."

* H. C. McMILLAN (*Proc. Inst. Cleveland Eng.*, January, 1903) recommended that the ratio between air and gas chambers should be 1.37 : 1.

Denk* states that it is not necessary to have a temperature in the regenerators of more than $800^{\circ}\text{C}.$, for with 25 per cent. excess of air and a gas with 25 per cent. carbon monoxide, both gas and air being pre-heated to $540^{\circ}\text{C}.$, the theoretical temperature of combustion would be $1750^{\circ}\text{C}.$, corresponding to an actual flame temperature of about $1480^{\circ}\text{C}.$ If the percentage of carbon monoxide were below twenty-five, a slight increase in the temperature of the regenerator would make up the deficiency in heating value.

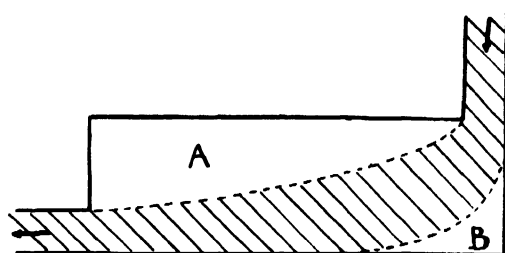


FIG. 135.—BAD SHAPE FOR CHECKER CHAMBER.

For the efficient working of regenerators it was further recommended that reversals should be made at regular intervals, the intervals not being too long; sizes of valves and chambers should be carefully calculated and the walls of the chambers and furnace watched carefully to avoid the presence of cracks and holes.

(273) **The Furnace Proper.**—The "furnace" is limited by the entry and exit ports, and is the place where the glass is melted by the completion of the combustion of the gaseous fuel induced by the introduction of the secondary air.

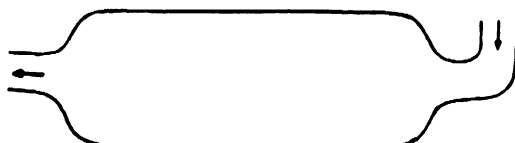


FIG. 136.—GOOD SHAPE FOR CHECKER CHAMBER.

It is not proposed, at this stage, to deal with furnace design, but just to give a few general ideas of glass furnace construction. The whole volume of the furnace interior should be such as to allow the velocities of the gaseous currents to decrease very considerably as they issue from the ports, allowing the products of combustion to remain as long as practicable in the furnace. Increase in time of sojourn of the gases in the furnace, in general, tends to better combustion, but if burnt gases are allowed to remain too long in the furnace then there is a decrease in temperature and efficiency.

* *Loc. cit.*

Two points which affect the time the gases remain in the furnace are the disposition of the ports and the height of the roof above the level of the glass. The height of the roof may be varied considerably within certain limits, and furnaces with quite high roofs or crowns have given good results for glass-making.

The disposition of the ports should be such as to obtain the most uniform distribution of temperature and avoid any intense local heating. This is particularly important in pot furnaces, since local heating may result in cracked pots. In any case local heating, however intense, does not assist the efficient working of the furnace. The ports in pot furnaces are placed frequently in the floor of the furnace, also in a central column, or in pillars of the end or side walls; the ports, almost invariably, are as near to the floor of the furnace as possible.

In tank furnaces the ports may be placed in the side walls of the furnace or in the end walls. The first arrangement gives a furnace of the cross-flame type, whilst the second gives one of the horseshoe flame type. The ports are usually placed as near to the glass level as possible in order to give the greatest heating efficiency.

Tank furnaces vary considerably in size, and in Britain it is customary to refer to the size of the furnace in terms of its dead-weight capacity, but in America it is rated according to its daily output.

The output possible from a tank furnace depends on the size and power of the melting end of the furnace and on the rate at which the metal melted can be worked out into useful ware.* The second factor is partly a question of size of the article made, partly one of the use of machinery. In regard to the former, American practice regards the size of the melting end as that dominating the capacity. The working end can be varied to suit particular needs, and, indeed, considerable variation is found. As a standard practice, the Owens Bottle Co. suggests a melting area of 17 square feet per ton of glass melted daily. At a number of works this power is easily exceeded. Thus, at one, the average output corresponds to 1 ton for each 11 square feet, and at two, the melting power is as high as 1 ton per 8 square feet.

In regard to depth, window-glass tank practice appears to be different from that for other types of glass. From observation of four window-glass tanks, Turner found the average depth to be as much as 5 feet. For most other glass, such as bottles, a standard appears to have been reached. H. L. Dixon has, after much experiment, settled on 3 feet 6 inches as the most suitable depth for the tank. Instances of tanks 3 feet, or even less, are found, but almost everywhere, whatever the length and breadth, the depth is 42 inches.†

The furnaces only 10 feet wide are usually found to be too narrow, and the regenerators become overheated. In the majority of cases it will be seen that the breadth is very roughly two-thirds of the length of the melting end.

The size of the working end is more or less a matter of convenience, depending partly on the means adopted to work out the metal. The

* *J. Soc. Glass Tech.*, 1919, 2, 166.

† H. TEISEN states that on the Continent the standard depth of bottle tanks is 1 metre or 3 feet 3 inches.

tenth furnace on the list below has a working end the internal dimensions of which are 16 feet across the bridge and 18 feet from the bridge to the nose. This, however, represents an unusual example, although a furnace with a proportionately still longer working end is in operation.

The following dimensions of the melting sections of some tank furnaces seen in operation, together with output where ascertainable, will illustrate the foregoing remarks:

<i>Length.</i>	<i>Breadth.</i>	<i>Depth.</i>	<i>Daily Output.</i>	<i>Mode of Operation.</i>
<i>Ft.</i>	<i>Ft.</i>	<i>Ft. In.</i>	<i>Tons.</i>	
34	24	2 9	50	Owens
32	20	2 6	—	—
20	14	—	15 to 18	Hand
20	16	—	30 „ 40	S. Automatic. Aut. Feed
25	16	—	—	Owens
45	20	—	80	—
32	16	3 6	105 to 120 per week	Semi-Aut.
38	25	3 6	—	—
14	12	3 8	24 tons	„
32	14	4 0	60 „	„
12	10	3 6	18 „	„
32	20	3 6	57 „	Automatic feed
15	10	—	—	—

(274) **Furnace Refractories.**—Refractories in general have already been dealt with, but at this stage it will be well if we consider the special properties required of refractories for use in glass furnaces.

For the bottoms and sides of tank furnaces are required materials which will not only offer high resistance to deformation through the action of heat alone, but also resist chemical attack both by batch materials and the glass, and they must also possess sufficient mechanical strength to resist the abrasive action due to the washing effect of heavy weights of fused materials. Large blocks are used very frequently in the construction of the sides and bottoms of tank furnaces. The blocks are made of "firestone" (mainly Durham) or fireclay. Opinion differs, but it is most generally held that the firestone blocks are preferable for the bottom and the sides of the tank below the actual level of the glass, whilst fireclay blocks are most suitable for resisting attack at the surface level of the glass. The blocks should be set with the "grain" at right angles to the flow of the metal. If set parallel to this flow, spalling is liable to occur, and plates of stone break away from the surface.

Corrosion is greatest at the melting end of the tank, where stones, blocks, or bricks are exposed to the action of fused alkalis before these enter fully into combination with the sand. With firestone the corrosion is generally very regular and "pitting" does not occur to the same extent as with many varieties of fireclay blocks.

The fewer the joints in the furnace structure the better, stronger, and more compact is the furnace; hence the use of large blocks. When fireclay blocks are used, however, it must be remembered that it is much easier and less expensive to prepare really sound small blocks than it is

to prepare large blocks of the same quality. Further, a furnace built of small blocks is more elastic—that is, it withstands expansion and contraction better, whilst cracks in joints are more easily remedied than cracks in large blocks.

For the roofs or crowns of glass furnaces silica bricks are now very largely used. The texture of the brick is, as has already been pointed out, a very important factor. The coarser-grained, open-textured bricks will resist sudden changes of temperature better, but will be more susceptible to the penetrating action of fluxes such as the dust from the glass batch. The fine-texture bricks resist the abrasive action of hot gases and the attack of fluxes better than bricks of coarse texture.

Whilst silica bricks expand, fireclay usually expands at first and then contracts to less than the original volume. The size and shape of the furnace are maintained by tightening or slackening bolts on long and cross tie-bars. It is very essential that careful attention be given to these bars during the heating up or cooling down of a furnace to avoid distortion of, or cracks in, the furnace walls and crown.

Though one pound of mortar per brick (9 ins. \times 4.5 ins. \times 3 ins.) is the bricklayer's normal maxim, in the building of furnaces, 250 to 300 pounds of fireclay or silica cement are enough to lay 1,000 bricks. The joints in silica structures may be larger than in fireclay, since silica expands and tightens the joints. The cement, fireclay or silica, should be used in the form of a thick cream, good fitting blocks or bricks employed, and excess cement squeezed out from between the blocks by rubbing one upon the other or by hammering. It is, of course, of paramount importance that the cement used be of the same refractory nature as the bricks or blocks. For closing all cracks in bricks, blocks, or joints on the outside of the furnace it should be washed, whilst warm, with a mixture of clay and sodium silicate. The amount of sodium silicate used should be the minimum amount required to obtain an easily applied "paint."

The thickness of the walls depends upon a number of factors. The loss by conduction through the walls and crown of a furnace may be represented by the following equation:

where

- Q = quantity of heat.
- T_1 = temperature of the inside of the furnace.
- T_2 = temperature of the outside of the furnace.
- r = thickness of the wall.
- A = area of the wall.
- t = time.
- K = thermal conductivity of the material.

For efficiency, K and the ratio $\frac{A}{r}$ should be kept as low as possible.

The first (K) offers no particular difficulty, but the second ($\frac{A}{r}$), though easily arranged theoretically, is not always reduced easily in practice.

The thicker the wall, the greater the amount of heat retained in the furnace and walls, and the greater is the consequent strain upon the refractoriness of the brick. As a result furnace walls are built thinner than is justifiable theoretically, since it is more economical in the end to spare the refractories and lose some heat. Water cooling has been applied to glass furnace walls but is very costly.

The value $(T_1 - T_2)$ may be reduced by passing waste hot gases around the outside of the furnace, but again the value of this procedure must be considered side by side with the cost of the arrangements necessary for performing it.

(275) **The Ports.**—The ports of a furnace—*i.e.*, the openings whereby the gas, air, and waste products enter or leave the furnace—vary largely in design and disposition. Some are very simple, others are complicated. When the gas and air are, as is usually the case, highly preheated, it is not necessary to go into great refinements of construction in order to secure complete combustion. Ports have essentially to withstand severe conditions, and their construction should permit of long life and easy repair.

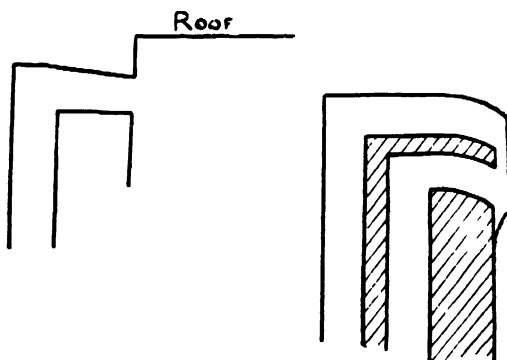


FIG. 137.—FURNACE PORTS

Siemens suggested shapes such as are shown in Fig. 137, in order to prevent gas from coming into contact with the roof or furnace sides. The air ports should be above the gas ports, and preferably overlapping them at both ends.* For small furnaces the ports should be inclined towards each other or the air ports given a sharp angle towards the gas ports, whilst for large furnaces, say 50 tons or over, the air port need only be given a slight angle towards the gas port.

Siemens further suggested that the meeting-point of the gas and air currents should neither be too near the ports nor too far away. In the first case, the ports suffer exceedingly from corrosion by the flame, and in the second case combustion would hardly have begun before the flame met the glass or glass-making materials, and would not exert its maximum heating effect. Where the gas and air meet far behind the port, very active corrosion of the port occurs, and there would appear to be little

* This is only possible in end port furnaces—*i.e.*, horse-shoe flame type.

justification for this procedure except where gas or air, or both, are fairly cool. However, mixing of the gas and air cannot be too long delayed, as combustion might be delayed also, and a cold furnace side result. A wash of the carborundum-clay mixture, previously mentioned, adds to the life of the ports.

The Amsler-Morton Company of Pittsburg, Pa., have patented a "high duty port" (see Fig. 138), which deserves some consideration. In tank furnaces in particular the chief mode of transference of heat from flame to glass is by radiation. To secure the best results certain conditions are necessary.

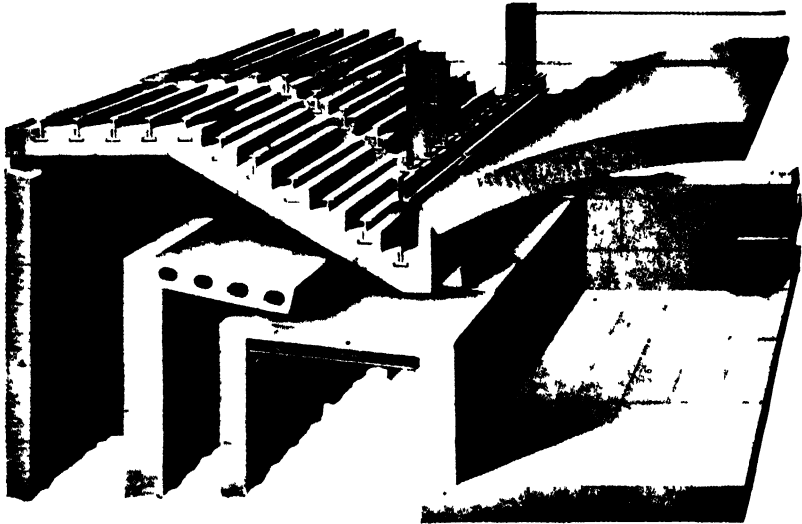


FIG 138 —THE " AMSLER-MORTON " HIGH DUTY PORT.
(By courtesy of the Amsler-Morton Company, Pittsburg, Pa)

In the first place the flame should be brought as near the glass as possible, for the transfer by radiation is inversely proportioned to square of the distance between source and destination. That is, if the distance is doubled the radiation intensity is only one-fourth as great. This applies to the top of the flame, as well as the bottom, as radiation takes place in all directions and the flame will permit radiation through itself. Thus the flame should hug the glass bath in the form of a sheet.

It will be obvious that if the whole surface could be covered with such a sheet, heat transfer would take place more rapidly, and consequently more economically, as the gases would transfer a greater quantity of heat to the glass than if a comparatively small portion of the surface were subjected to the action of a few deep streams of flame.

To secure such a sheet of flame, it is necessary that the ports of the furnace be low and broad and directed towards the bath, and that the distance between the gas and air ports be made as small as possible.

The " Amsler-Morton " High Duty Port is designed to meet these conditions, and in practice it is claimed that it does so. The proportions have

been carefully worked out for various areas of melting surface, so that the quantities of air and gas are just right to produce complete combustion, with minimum excess air. This produces maximum practical temperature in a thin sheet of flame over a greater area of the glass. Fuel consumptions are stated to have been reduced as much as 29 per cent., and capacities of tank furnaces increased as much as 25 per cent.

The relative sizes of gas and air ports requisite for efficiency may be calculated. When the temperature of the incoming gases, composition of the fuel gas, and the quantity of excess air needed for complete combustion are known, the relative sizes of the ports may be obtained, neglecting small pressure differences in the furnace system, for producing equal velocities of gas and air at the ports. Examples of the calculation are given below:

<i>Composition of Producer Gas (by Volume).</i>						<i>Theoretical Volume of Oxygen Required.</i>	
Carbon monoxide	24.2 parts	..	12.1 parts
Hydrogen	8.2 "	..	4.1 "
Methane	2.2 "	..	4.4 "
Carbon dioxide	4.2 "	..	—
Nitrogen	61.2 "	..	—
Totals ..						100.0 "	20.6 "

Therefore the volume of air theoretically required = $\frac{20.6 \times 100}{21} = 100$ parts approx.), with gas and air at the same temperature.

The volume with 25 per cent. excess air = 125 parts.

Therefore the relation between volumes of air and gas = $\frac{125}{100} = \frac{5}{4}$.

Thus the relative sizes of gas and air ports, using 25 per cent. excess air, are as 4 is to 5.

With 50 per cent. excess air the ratio is 2 to 3.

With gas produced by the modern steam-blown gas producers and containing about 27 per cent. CO, 14 per cent. H₂, and 4 per cent. CH₄, the ratios are about—

$$\frac{1.7}{1.0} \left(\frac{\text{air}}{\text{gas}} \right) \text{—for 25 per cent. excess air.}$$

$$\frac{2}{1} \left(\frac{\text{air}}{\text{gas}} \right) \text{—for 50 per cent. excess air.}$$

(276) **The Chimney.**—The chimney is the draught apparatus for discharging into the atmosphere the products of combustion and of insuring at the same time the circulation of the various gas currents, either from the furnace alone or also from the producer. It begins where the regenerative or recuperative chambers end, in the former case at the reversal valves. The draught must be sufficient to exert a pulling influence on the flames at about the centre of the furnace, and draw them through the ports in the case of the cross-flame furnace. It must also be sufficient to overcome the friction in the regenerators and flues.

The intensity of the draught depends upon the temperature of the products of combustion when they leave the checker chambers, and upon

the height of the chimney. The temperature of the gases at the bottom of the stack should not exceed 200°C . A chimney height (taken from the level of the producer grate to the summit of the stack) of 90 to 100 feet is ample for a furnace with a dead capacity of 150 tons.

The requisite diameter and height of the stack can be calculated, given the necessary data relating to volume and temperature conditions of the waste products and the pressure conditions inside and outside the furnace system. Since the greatest heat loss in the furnace system is that in the waste products which pass up the chimney it is essential that strict attention be paid to chimney problems. The actual loss of heat energy up the chimney depends upon (a) the temperature of the products of combustion, (b) the amount of unburnt fuel in the combustion products, and (c) the amount of excess air in the same products. All these three factors can easily be kept under control, and in most glassworks saving of fuel could be effected by a little attention bestowed upon the last portion of the furnace system.

(277) **The Gaseous Currents in the Furnace System.**—Through the whole furnace system the currents of gases should be controlled by dampers, or valves of some kind. In general, the greater the number of regulating devices the more easy and efficient should be the control of the furnace. If the dimensions of flues, checker-chambers, etc., are known and adequate temperature and pressure readings are taken, the most efficient conditions in all parts of the plant can be determined. Unfortunately this feature of furnace practice has been sadly neglected, and information relating thereto is very scanty. Toldt* gives the following figures for the maximum allowable velocities in various parts of regenerative furnaces:

Air or gas through valves	3.5 metres per second.
Air or gas entering checker chambers	3.0 " "
Mean velocity of air or gas through checker chambers	1.0 " "
Gas issuing through ports	8.0 " "
Products of combustion through the furnace.. .. .	2.0 " "

If a furnace be designed in accordance with Toldt's figures, the minimum cross-sectional area of any of the parts can be calculated from the above figures once the required rate of production of gas has been decided upon, and also the approximate temperature of the gas and air leaving the regenerators.

In Table XCVII. are figures given by Le Chatelier† for the minimum times of sojourn of gas and air in various parts of a regenerative furnace, working at the temperatures given in Table XCVIII.

TABLE XCVII.—TIMES GASES SHOULD REMAIN IN VARIOUS PARTS OF FURNACES.

Gas in regenerator	4 seconds
„ checkerwork	3 „
Air in regenerator	5 „
„ checkerwork	3 „
Products of combustion in the furnace	2 „

* F. TOLDT, *Regenerativ Gasöfen*, p. 262.

† *Compt. rend.*, 1892, 114, 470.

TABLE XCVIII.—TEMPERATURES OF VARIOUS PARTS OF FURNACES.

					<i>Degrees C.</i>
Gas in flue from valve to regenerator	400
Air " " " "	270
Air at valve	30
Mean temperature of gas in regenerator	625
" " " air "	610
Gas leaving regenerator	850
Air " " " "	950
Products of combustion entering regenerator	1600
" " " passing through valves	300

The velocities and times of sojourn will vary with the temperatures.

CHAPTER XXVII

GAS-FIRED FURNACES—RECUPERATIVE

(278) **Pot Furnaces.**—During recent years pot furnaces of the recuperative type have come largely into use. In principle, recuperative preheating consists in passing the gas to be heated through a tube or narrow chamber around which the hot waste gases are circulating. By this means heat is conducted through the dividing walls from hot to cold gas. Recuperative heating is continuous, requiring no reversal, and one set of chambers only. In practice it is found most convenient to preheat secondary air only and conduct the hot producer gases directly into the furnace. It will be seen that this process is much simpler in design than regenerative preheating, but it is not without difficulty in application. The lack of conductivity of heat of recuperator walls, the tendency for these to crack and allow air and waste gas to mix, are some of the problems inherent with this type of furnace.

Before describing the more common type of recuperative furnaces—*i.e.*, those which are gas-fired—we may profitably consider one which may be termed a semi-direct-fired furnace with recuperation.

(279) **The “Dennis-Simplex” Furnace.**—In describing this furnace and its origin we have quoted very fully from an article* by Travers, since the development of the furnace is a very interesting feature in modern glass furnace practice.

In the glass works in which the “Dennis-Simplex” furnace originated there were, up to the middle of 1919, furnaces of two types. Three of the furnaces were so-called direct-fired pot furnaces fitted with Frisbie under-feed arrangements. There was also a gas-fired furnace of a Continental pattern, with two producers built into the centre of it, and flanked by recuperators. The gas from the producers rose through a central eye, meeting the hot secondary air from the recuperators at a little distance below the sieve. The pots, eight in number, stood in a circle about the eye, and the products of combustion passed between these pots, through openings in the pillars supporting the crown, and thence, downwards, into flues leading to the recuperators. In this furnace very intense combustion took place in the eye and behind the pots, and for this and other reasons the furnace did not prove a satisfactory one. Finally one of the flues collapsed, one of the recuperators became full of glass, and the furnace was put out of action. It was decided not to rebuild the furnace, but as there was an urgent demand for glass, the management

* *J. Soc. Glass Tech.*, 1920, 4, 205.

decided, at all events as a temporary measure, to reconstruct it, replacing the producers, which were to be cut away entirely, by a Frisbie under-feed grate. When the furnace was fired up, it was found to work with astonishing efficiency, and to be extremely easy to operate.

A section through the furnace is shown in Fig. 139, and it will be seen that the grate is fixed below a conical space which tapers upwards to the eye. The centre of the grate is occupied by the underfeed arrangement, which consists of a solid frame with a conical cavity, and through the cavity the fuel is forced by means of a piston. Therefore, after each firing, the space remains filled with coal. The weight of each

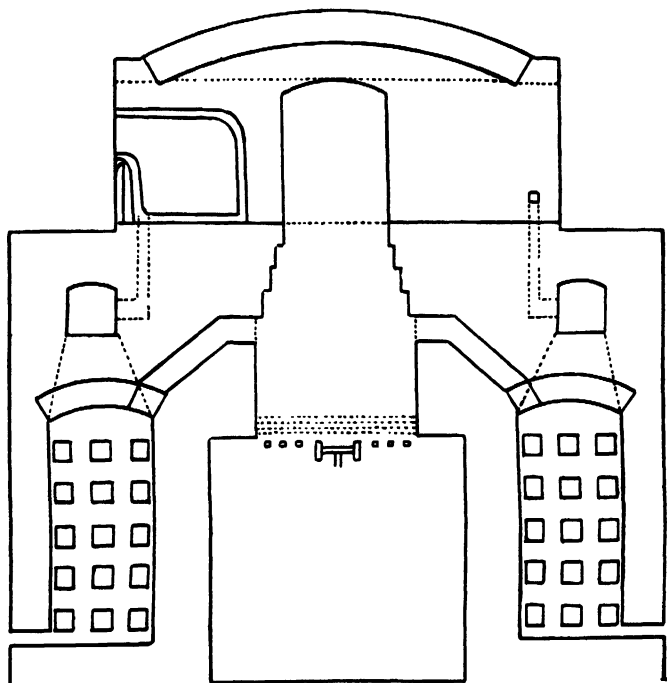


FIG. 139.—THE "DENNIS-SIMPLEX" FURNACE.

charge is from twenty to twenty-five pounds, and about four charges are put up into the furnace every forty-five minutes, the rate of firing being about 130 pounds of fuel per hour. Each charge of fuel is introduced below the partly gasified fuel of the previous charges, and, as in the case of the Jones under-fed grate, the products of distillation from the fresh fuel pass through a red-hot layer, and, in the process, the tarry matter and heavy hydrocarbons are to a large extent decomposed. The partly carbonised fuel is pushed outwards over the grate bars, and the coke is gasified by the air passing through it. The depth of the fuel bed is from 6 to 9 inches, yet gasification of the fuel is sufficiently complete.

The secondary air enters at the sides of the conical space and at a

depth of about 2 feet 6 inches below the eye. However, it seems to be perfectly clear that combustion does not take place below the sieve, for the temperature in the conical space is not above a bright red heat, while that of the furnace chamber is a full white heat. Practically no clinker is formed on the grate or about the sides of it. The fire is rarely cleaned more often than once in twenty-four hours, and is not broken up, or indeed touched at all, between the times of cleaning.

The total weekly consumption of fuel in the furnace, over a period of nine months, rarely exceeded a total quantity of 9.25 tons. There was an output of over one ton of metal worked out for one ton of fuel consumed, when a soda-lead glass was melted. It was estimated that, working at fuel capacity, the furnace would give two tons of glass per ton of coal for a working week of only five days.

Direct-fired furnaces with the Frisbie feed in the same works were burning the following quantities of coal, of better quality, each week, and required a longer time to plain the metal:

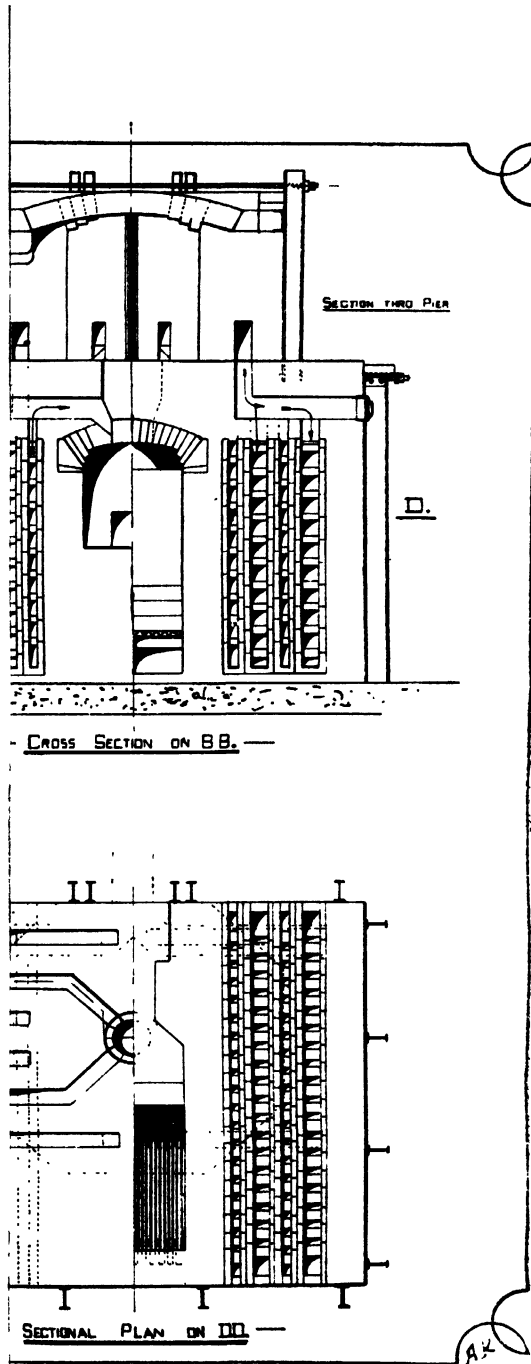
An 8-pot furnace	30 tons.
A 10-pot	40 ..
A 12-pot	nearly 50 ..

The high thermal efficiency of the Dennis-Simplex furnace appears to be due to the fact that, apart from recuperation, the furnace works under a positive pressure.* In this respect it is noteworthy that the furnace is so constructed that in virtue of the height of the secondary air port and the mean temperature in the recuperators, the secondary air has a positive pressure equivalent to 1.6 millimetres of water at the secondary air port under the eye. The pressure of the gases from the grate at this point is about 0.9 millimetre of water. Hence the chimney damper can be closed sufficiently to produce a back pressure up to, say, 0.8 millimetre of water in the combustion chamber. This allows the flame to play all over the furnace instead of being drawn through in more or less stream line directions. Moreover, cold air does not leak into the furnace through working holes and cracks. In addition, it is obvious that the ratio of the secondary air to the primary air can be regulated by merely closing the air slides leading into the recuperators.

The hot secondary air enters the furnace at a comparatively low velocity in the form of an annular stream surrounding, but not actually in contact with, the gas stream, which is of comparatively small cross-section. The latter is moving relatively faster and acts as a suction jet. Mixing of gas and air therefore takes place fairly evenly and slowly during the passage of gases through the furnace. This avoids high intensity and local heating. As a consequence the eye of the furnace and the backs of pots do not wear out so soon, and the life, and therefore the efficiency, of each is longer than when quick mixing occurs in the eye.

(280) A "**Simon-Carves**" Furnace.—Turning to gas-fired furnaces, Fig. 140 shows sectional views of a glass pot furnace designed by Messrs. Simon-Carves, Ltd. The furnace is of the continuous, recuperative type, which eliminates the reversing of the flue gases and secondary air essential with the regenerative type of furnace. The recuperators are formed of

* See description of the "Stein" and "Hermansen" furnaces



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narrow vertical flues with thin partition walls constructed of specially designed tiles, and are built to give a constant flow of the waste gases and secondary air. Uniform temperatures are thus maintained. The design of the recuperator gives the minimum of frictional resistance to the flue gases, and the special bonding of the flue tiles prevents any possibility of short-circuiting.

The flue gases are regulated from the bottom of the setting just before their exit into the chimney flue, and the dampers are placed adjacent to the secondary air slides, so that the working of the furnace is controlled from one position at the front of the setting. No forced draught is necessary, an ordinary chimney being quite suitable. Owing to the simplicity of the design, waste gas and air flues are completely visible and accessible for their entire length for inspection and cleaning purposes.

Each setting is self-contained with its own producer, thereby economising fuel as against the regenerative type, where the gases are transmitted from a central producer. Fuel costs can be further reduced by the use of gas coke for firing the producer.

The furnace shown in Fig. 140 contains 4 pots and 4 waste gas flues—viz., one flue to each pot, so that each pot is controlled by its own flue independently of the regulation of the others. Thus any pot or pots may (when required) be maintained at melting temperature, whilst the others continue at working temperature.

Ground space is economised by the compactness of the arrangement, and a further saving is effected in the attention required during operation due to the absence of periodical gas reversion which is necessary in the usual type of melting furnaces. For the same reason the life of the pots is increased, the temperature being much more regular, while the general efficiency is equal to that of the regenerative type.

Furnaces suitable for 4, 8, or more pots can be constructed, according to the capacity required, and pots may be either open or closed type, as desired.

(281) **The "Stein" Recuperative Pot Furnace.**—Messrs. Stein and Atkinson, Ltd., the designers and constructors of the "Stein" furnace, use a recuperator of exclusive design. Before dealing with the furnace, therefore, it will be better if we first consider the design of the recuperator. J. S. Atkinson* claims that with a proper design of recuperator, and conditions allowing of its application, results can be obtained which surpass very considerably all regenerator applications. Moreover, the construction of the whole furnace is much simplified, and a degree of working control, as regards furnace temperature and atmosphere, is obtained which cannot be approached with regenerative furnaces.

Atkinson states that the principal causes of failure in faultily designed recuperators are the following:

(1) Short circuits between the air passages and the passages through which the products of combustion pass. Also short circuits between the gas and the products of combustion, in cases where the gas is also preheated. Such short circuits are caused through leaky joints, and result in a proportion of the air for combustion, and the gas—where this is preheated—being passed directly to the chimney flue without entering

* *Reprint from J. West of Scotland Iron and Steel Inst., Session 1921-22*

the furnace proper. If leakages are at all extensive, the proper heat cannot be obtained in the furnace, or this heat can only be assured by an excessive gas consumption.

(2) Owing to excessive thickness of the partition walls between the air passages and the waste gas passages, the transfer of heat from the waste gases to the air is very imperfect. The same applies to the preheating of the gas when this is also passed through the recuperators.

(3) One frequently finds recuperators having horizontal air passages for the preheating of the air. This method is wrong, both in theory and in practice. Without forced draught the air can only be drawn through the horizontal passages in the recuperator by the chimney draught. This causes very faulty furnace operation, as it necessitates the flame pressure passing over the furnace bed being maintained appreciably below atmospheric pressure, resulting in irregular heating of the charge, owing to the flame taking the shortest cut across the furnace bed, from inlet to outlet ports, instead of spreading out over the whole area of the bed, as it will do if its pressure is maintained slightly above atmospheric pressure. Also with the flame pressure below atmospheric pressure, there is a continual filtration of cold atmospheric air into the furnace through brickwork crevices and imperfectly fitting doors, causing loss in temperature and excessive oxidation of the material heated.

(4) All systems of forced draught for recuperation are contrary to the principle of good working, as their provision is an unnecessary expense; short-circuiting, through leaky joints, is promoted, and it is impossible to maintain the very slight but very necessary positive flame pressure required for good working.

The "Stein" system of recuperation has been applied with great success to a very large number of different types of furnaces, and Atkinson claims that it overcomes all the faults referred to above.

Fig. 141 shows a view, in perspective, of the "Stein" recuperator. The recuperator is built up of special-shaped firebrick blocks. The air passes up through a very large number of vertical passages of small section, and the waste gases pass horizontally and in a zig-zag manner through the flues formed between the recuperator blocks. The width across the air passages is only about one inch and a half. The result of this is, that each particle of air comes in contact with, or scrubs, the incandescent refractory partition between the air passages and the flues for the waste gases; moreover, owing to the small thickness of these partition walls, about three-quarters of an inch, the air picks up the maximum amount of heat possible. In practice, it is found that the air is heated to within 150° to 200° C. of the temperature of the waste gases as they enter the recuperator.

The total combined area of the vertical air passages is very much in excess of the area of the air inlet and air outlet passages from the recuperator, consequently the air remains in the recuperator for a lengthy period, virtually coming to rest, thus allowing time for the exchange of the heat from the waste gases to the air through the thin refractory partitions.

In the "Stein" recuperator, the only joints through which leakage of the air into the waste gases could take place are horizontal; these

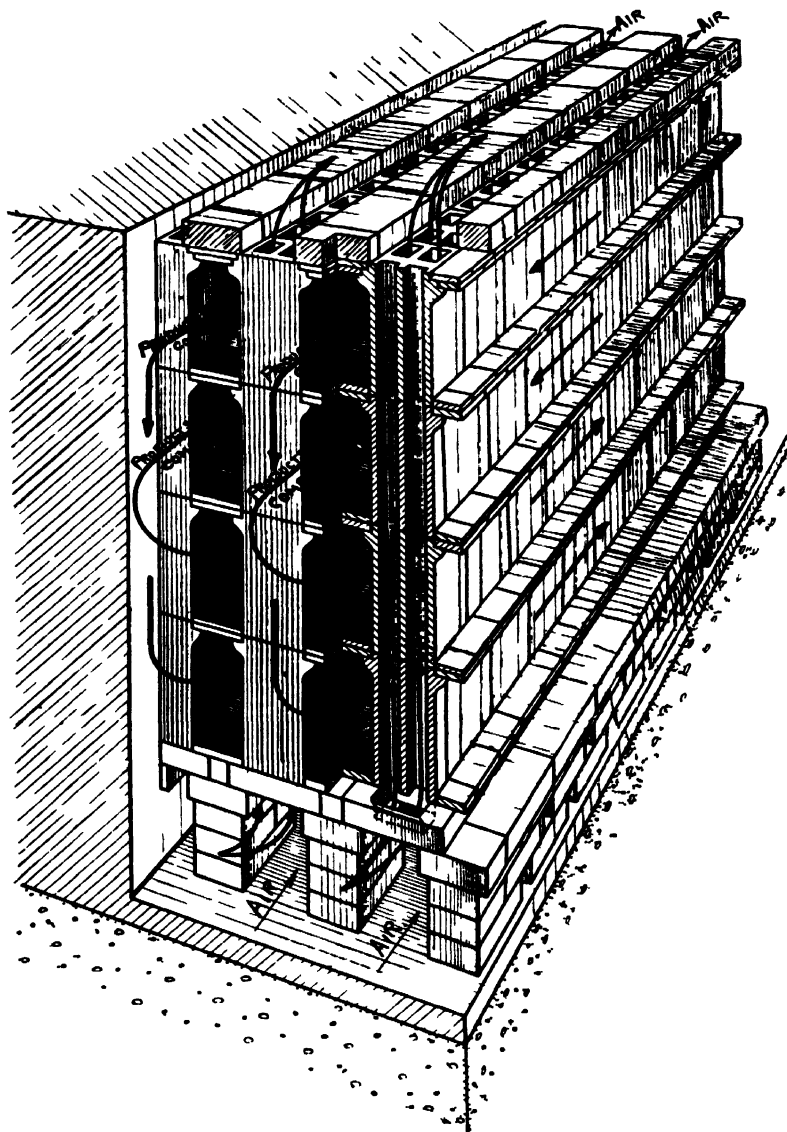


FIG 141 —THE "STEIN" RECUPERATOR
(By courtesy of Messrs Stein and Atkinson, Ltd, London)

joints naturally tend to keep tight, owing to the weight of the recuperator blocks themselves. Another feature which eliminates risk of leakage is that the pressure of the air is practically in balance with the pressure of the waste gases throughout the full length, from top to bottom, of the recuperator, so that there is very little or no tendency to leakage, even assuming faulty joints.

The air is heated on passing up through the vertical passages, and is rarefied, becoming lighter than the atmospheric air. This, combined with proper regulation of the chimney damper, gives a positive air pressure above the atmospheric. This positive air pressure, coupled with a positive gas pressure, permits of the flame pressure being maintained slightly above the atmospheric pressure in the furnace. Such a condition, for the reason pointed out above, is most essential for good furnace operation.

No forced draught is necessary, and the total air for combustion is controlled by adjustable air inlet valves, or shutters, situated at the base of the recuperator. If a slight reducing atmosphere is required in the furnace, the air supply is reduced until there is a slight insufficiency for complete combustion of the gas.

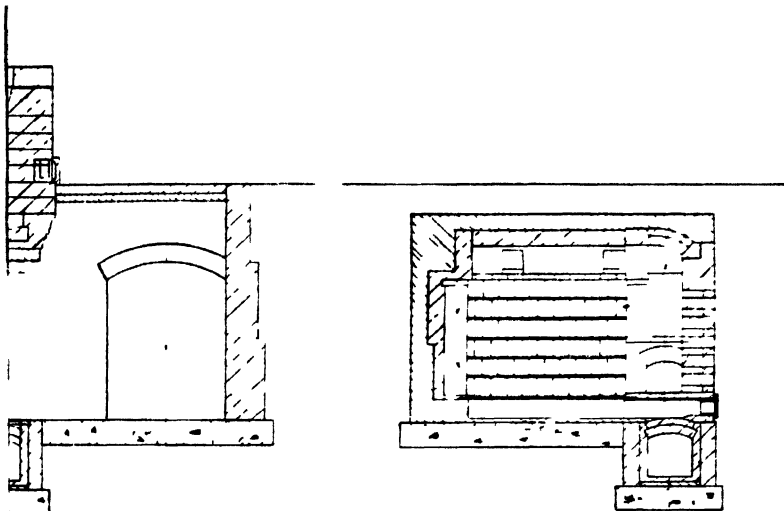
In Fig. 142* is shown the "Stein" recuperative pot furnace, installed at the works of Messrs. Houdaille and Triquet, Choisy-le-Roi, near Paris, by Messrs. Stein and Atkinson. The recuperative chambers are placed on either side of the furnace, this arrangement allowing the recuperators to be entirely isolated for the flow of glass occurring in the event of a pot breaking. For the purpose of holding such glass, glass-pits are arranged, one at the bottom and one on each side of the central burner. The two side-pits are in connection with the flame outlet passages. In the event of a broken pot and the glass finding its way into the flame outlet passages and into the two outer pits, the glass is kept in a state of fusion right up to the stopper openings in the pits, as the flame follows the path of the glass. The gas may be supplied by independent producers, or the producers can be built attached to the furnaces.

In Table XCIX. the designers supply details of typical fuel consumption obtained in the above furnace.

TABLE XCIX.—FUEL CONSUMPTIONS IN THE "STEIN" FURNACE.

<i>Number of Pots.</i>	<i>Capacity of each Pot.</i>	<i>Coal Consumption of Furnace per Twenty-four Hours.</i>
	<i>(Tons)</i>	<i>(Tons.)</i>
6	990	3,300
6	1,540	3,960
8	990	4,180
8	1,540	4,840
10	990	4,840
10	1,540	5,720
12	990	5,500
12	1,540	6,300

* J S ATKINSON, *J. Soc. Glass Tech.*, 1919, 3, 148.



SECTION JJ

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Each pot in the furnaces mentioned in Table C. is stated by the firm to have been "cast and worked in 24 hours."

(282) **The Hermansen Recuperative Pot Furnace.***—A special feature of this furnace is again the type of recuperator. The latter consists of highly refractory tubes interlocking and built in bond both ways, so as to form a very compact and strong block, which completely fills the chamber in which it is built.

Fig. 143 shows the special tubes used. It will be seen that the air channels are arranged crosswise in relation to the waste gas flues. The

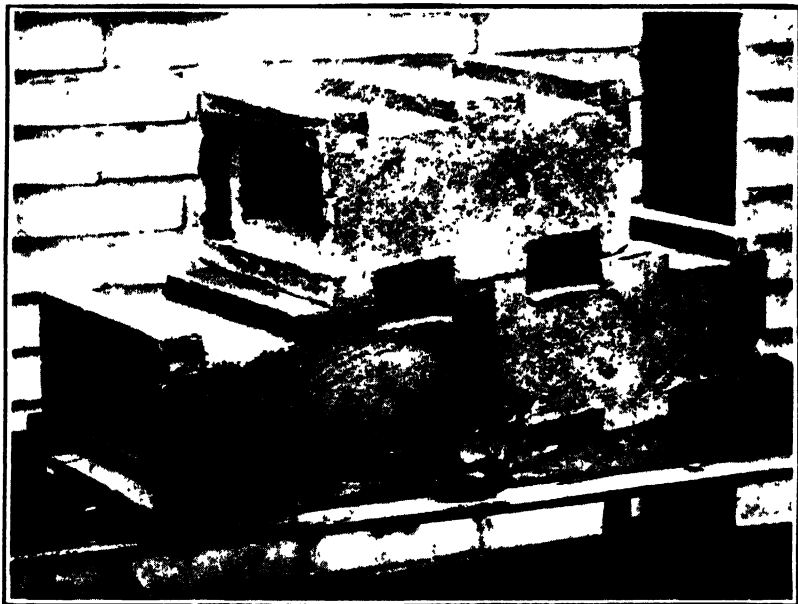


FIG. 143.—THE HERMANSEN RECUPERATOR TUBES.
(By courtesy of A. Hermansen, Esq., C.F., Birmingham.)

direction which an air or gas current has to take to enter respectively the waste gas or air flues is broken at least four times, thus giving a great safety against leakage.

Another feature of the recuperator is its accessibility. The waste gas flues can be cleaned all through their length by taking out a plug in the front. These plugs are provided with a small hole covered with a mica plate, so that the fireman can see at a glance whether the furnace is working normally or not. Both the waste gas and air usually take two, three, or more turns through the recuperator, depending on the size.

In order to work a recuperator with the highest economy it is necessary to have the air and gas passing through it at a fairly constant speed. The waste gas entering the top rows of the recuperator has a greater

* See TH. TEISEN, *J. Soc. Glass. Tech.*, 1917, 1, 74

volume than in the bottom rows, where the temperature is lower, and also, the cold secondary air entering the air chambers increases in volume as it rises. As the air and gas expand about four and a half times between normal temperature and 1000°C . it will readily be seen that in order to keep a constant speed through the recuperator, the sectional areas of the passages must be increased accordingly. It is evident that when the speed is kept in check the loss of positive pressure due to friction and change of direction can be made a negligible quantity. This is secured in the "Hermansen" furnace by arranging an increasing number of rows of passages as the air expands.

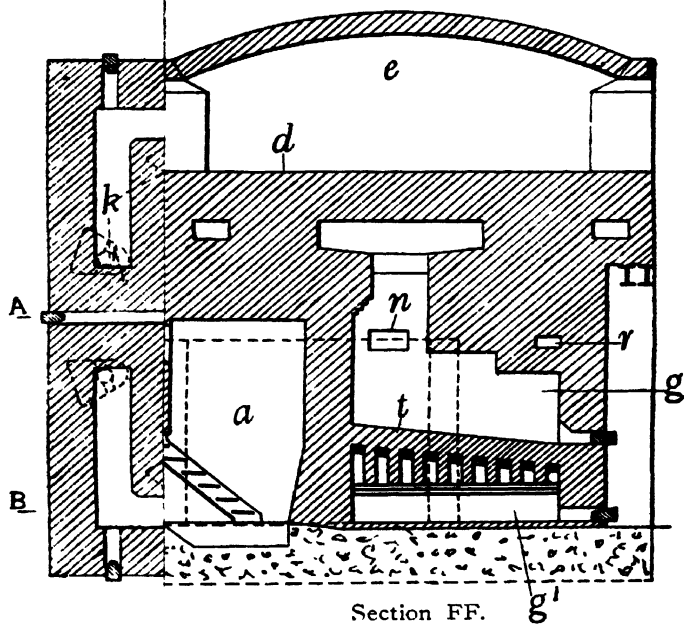
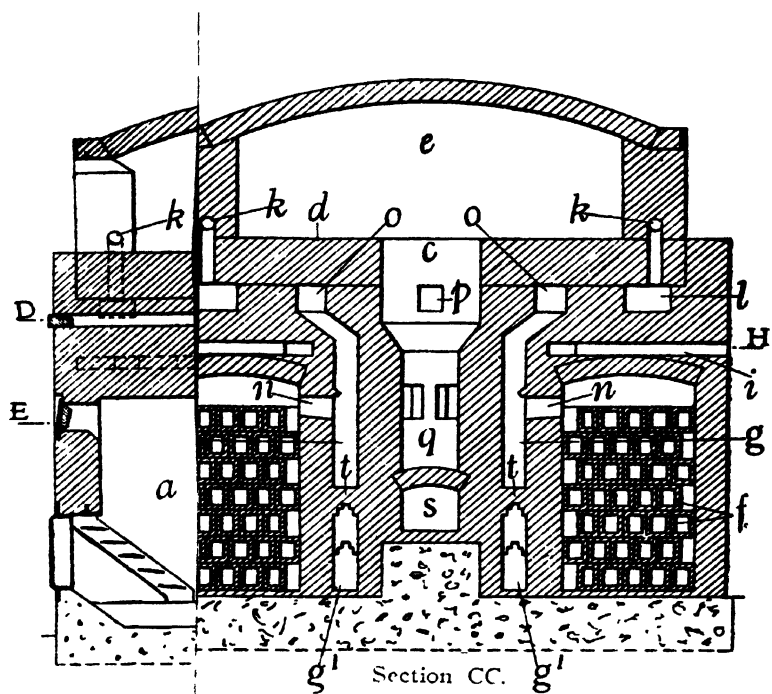
The Hermansen recuperators, when built well, are stated to last from six to ten years, which compares favourably with the checker work in the regenerative furnace, which has usually to be renewed every year on account of being choked with dust, if not for other reasons. Also, in the recent designs, the recuperators can be rebuilt without having to pull down any other part of the furnace.

A general complaint against the gas-fired furnace, whether regenerative or recuperative, is the leakage of molten glass through the brickwork, penetrating into and damaging the vulnerable parts such as regenerators and recuperators below the sieve, and, to prevent this, two different methods have been employed. One consists in placing the regenerators or recuperators outside the furnace, as in the "Stein" pattern; the other in isolating these parts in an efficient and safe manner.

(282A) **The "Teisen" Pot Furnace.**—An example of the second method is the furnace patented by Teisen and illustrated in Fig. 144. This shows a recuperative glass melting furnace fired by two step-grate producers (a) arranged centrally in the furnace and flanked on either side by a recuperator as usual. The glass from the producer enters a central burner (c), beneath which is arranged a glass pocket (q) into which glass from a broken pot will run. The glass pocket is of special design. It is of rather large capacity to allow a considerable quantity of spilt molten metal to stand over during melting so as not to upset the glass when fining.

Means for heating the glass pocket are provided, which is of special importance where the furnace gas is rather cold and where hard glass which easily solidifies is melted. A draw-off flue (r) at the end of the pocket leads the waste gas direct to the recuperator. Under ordinary working this is closed. The bottom of the glass pocket consists of arches or blocks with an air space below, which allows for cooling as required. This arrangement makes the repair of the pocket an easy matter, and any leakage of glass from the pocket is limited to flowing through the side walls to places where, as will be seen later, it can be readily trapped. In older designs the bottom was solid and the glass in time penetrated the brickwork, which in due course gave way, resulting in settlement of parts of the furnace and penetration of glass into the flues.

Over the recuperator there are a number of horizontal cooling channels (i), through which a certain controllable amount of cold air passes by natural draught, and these are projecting sufficiently far into the surrounding brickwork to stop effectively any molten glass from penetrating the arches over the recuperators.



At the side of the recuperators, between these on the one side of the burner and central waste glass pocket on the other side, are arranged special trap pockets or flues (*t* and *g*) which prevent glass from reaching the recuperator through the intermediate brickwork. These pockets are divided into an upper pocket, formed in the secondary air flue, in which molten glass flowing from the upper region of the burner may accumulate, instead of, as before, following the air flues down to the recuperator, and a lower one consisting of a system of vertical trap channels communicating with the horizontal flue or pocket, and acting as a trap for any sideways flow of glass from the central glass pocket.

Besides, in the special manner of its design, it acts as a safety pocket for the upper one, and adds considerable strength to the whole construction.

It will thus be seen that the recuperator is isolated in the following manner: (1) the bottom rests on the foundation; (2) the front and the one side extend to the outside; (3) the top is protected by a system of cooling channels (*i*), the back by a special glass pocket (*h*), and the remaining side partly by the producers and partly by the special pockets and trap flues (*t* and *g*). The result is that it is absolutely safe from any flow of glass.

It is a well-known fact that where direct-fired furnaces are replaced by the more efficient gas furnaces, working with either regeneration or recuperation of the secondary air, the higher flame temperature has often resulted in damage both to the blocks round the outlet of the burner as well as to the pots. The sudden combustion which takes place in a vertical burner with radial air inlets gives admittedly a very high local flame temperature which requires the highest quality of blocks and pots to withstand it, unless the flame temperature is reduced artificially by decreasing or increasing the amount of secondary air unduly, which, of course, does not agree with economical working.

In Teisen's burner the secondary air is admitted tangentially to the burner and is caused to swing round the gas stream, the latter entering from below and occupying the central portion of the burner. The combustion starts where the two streams meet, but between this preliminary region of combustion and the surface of the burner there is a lining of air which serves to protect the surface from the destructive action of the flame. The final mixing of the gas and air and the completion of combustion occurs first when the gases emerge from the burner, resulting in a uniform and widespread distribution of the temperature.

Whereas the edge of the burner is usually destroyed in a month or two, in a large 12-pot furnace recently built, which has been running for about six months at a temperature between 1400° C. and 1500° C. the edge round the burner is still perfect. This in spite of the fact that the furnace has been mostly worked with a secondary air supply of only 20 to 25 per cent. excess.

In the Teisen furnace the waste gases from the pot chamber are led away in the usual manner through holes provided in the pillars and arranged in front of the pots, from where they are distributed to two connecting waste gas channels (*l*) which end in the glass pockets (*h*) before the waste gas finally enters the recuperator. In this pocket the

glass which may penetrate the joints of the seat or pillars finds its way down and is taken out through a door at the side before reaching the recuperator.

THE OPERATION OF THE "TEISEN" FURNACE.—The furnace can be worked on two different main lines, that of continuous melting and working out, and that of day working, melting by night and working out during the day. In a 10-pot furnace with pots of 38 inches diameter, these are filled and the contents melted every night and

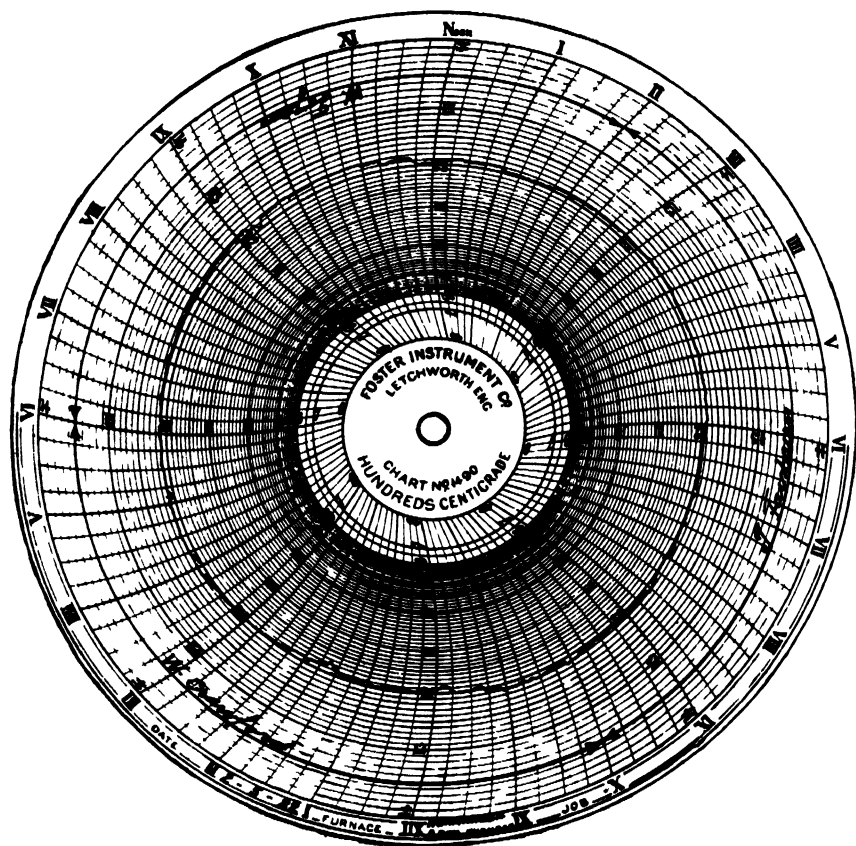


FIG 145—A "FOSTER" TEMPERATURE CHART FROM A HERMANSEN-TEISEN FURNACE PLANT.

worked out during the day, making lead metal for bulbs and tubing. This is the largest furnace which can be worked in such a manner; for larger furnaces the continuous process is necessary. During the melting period, which takes approximately 15 hours from the time of ceasing work to starting work, the producers are fired alternately every half-hour or hour, depending on the kind of coal used.

In this way a steady gas supply is ensured and the temperature increases more uniformly than if the producers were fired simultaneously. It is important to fire heavily in the beginning of the melting period to ensure a fairly rapid increase of temperature during this period; also, when the maximum temperature has been reached, to allow for the slowing down of the furnace at the right time, as otherwise it may run too hot and damage the pots. The cooling down to working temperature can be done in 3 to 4 hours. The producers are clinkered usually twice per 24 hours, and care is taken that they are well filled when the working out starts, in which case they need only have an occasional fire during the meal hours, which is of importance where open pots are used.

The furnace is usually worked by natural draught, the positive pressure of the gas in the producer and of the hot air in the recuperator being more than sufficient to maintain a correct balance in the pot chamber. To speed up the melting and to control unfavourable wind conditions of the chimney, the producer is sometimes blown by steam or by air. The latter works quite satisfactorily, as the step grate is water-cooled and evaporates a fair portion of water, thus saving the installation of a boiler.

Much has been said for and against the built-in producer as compared with the modern mechanical producer, and, as mentioned before, this furnace is adaptable for both types.

Where the furnaces are worked on the continuous system the working is, of course, much simplified, as it only consists of firing the producers regularly, and otherwise keeping the furnace at a constant temperature. The temperature chart (Fig. 145) shows an 8-pot furnace working on this method.

This system has been adapted to all sizes of furnaces, from small ones containing two or three pots of 3 cwt. each up to such containing twelve pots of the American 3,000-pound size. In the latter case the fuel consumption, when running the furnace between 1400° and 1500° C. and making three melts per week, was stated to amount to approximately four tons per day of a coal rather high in ash, which is nearly 50 per cent. lower than what is commonly used in regenerative furnaces in the United States.

To show the difference in working between a regenerative furnace and one of the continuous type, the curves shown in Fig. 146, taken from two furnaces working in exactly the same manner, the one only melting by day and the other by night, at Messrs. Philips' Glass Works, Eindhoven, Holland, may serve. It will be seen how steady the temperature of the recuperative furnace was as compared with the regenerative. Both were worked out from 8 to 5, with the first filling about 6 o'clock, the second at 9 o'clock, and the maximum temperature reached about 5 o'clock, leaving three hours for cooling. Lead-oxide containing glass for lamp bulbs was melted in both furnaces. The temperatures were registered on a double Cambridge recorder. It will be seen that the average temperature in the recuperative furnace is lower than that of the regenerative type, although the melting time is exactly the same.

(283) **Tank Furnaces—Recuperative.**—Shortly after the Siemens furnace had gained a fair footing in the glass industry, recuperative

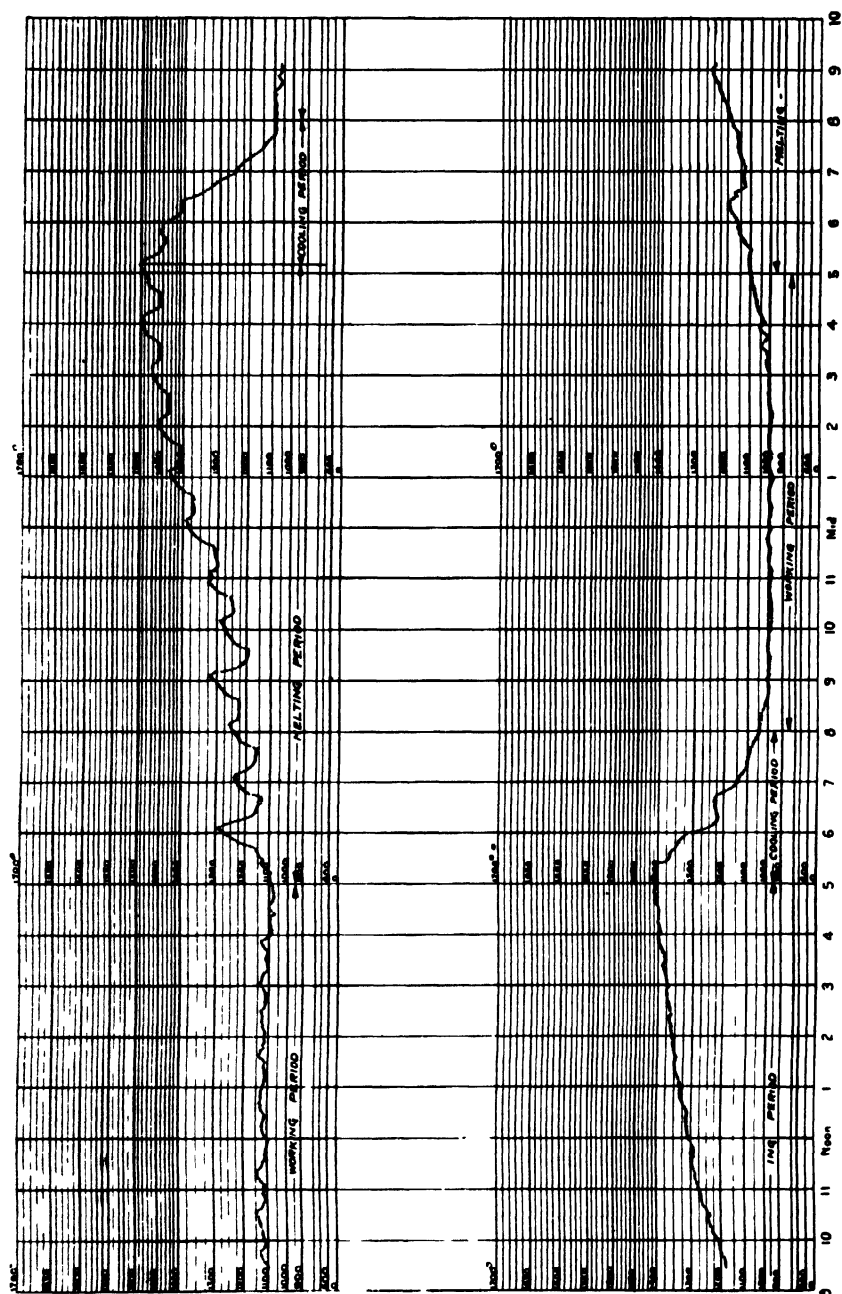


FIG. 146.—A "CAMBRIDGE" TEMPERATURE CHART SHOWING RECORDS OF TEMPERATURES FROM RECUPERATIVE AND REGENERATIVE FURNACES.

(By courtesy of A. Hermansen, Esq., C.E., Birmingham.)

tanks were introduced. Some were designed on the single horseshoe principle, whilst others, like the "Nehse-Dralle" and "Sticzinsky" furnaces, were operated on the double horseshoe system (see Fig. 147). Both single and double horseshoe systems lent themselves readily to the recuperative form of firing.

As regards efficiency and fuel consumption, there was little to choose between the regenerative and recuperative tanks, but the latter occupied less space and were less costly to erect owing to the reduced number of flues, valves, etc., required. The low cost of upkeep of the recuperative form may be judged from the following: Mr. Th. Teisen informed the authors that a "Nehse-Dralle" tank, which he inspected in 1919, had been working at a bottle works in Denmark for twenty-seven years, during which period the recuperators had been renewed only three times. The side blocks were usually replaced every eighteen months, whilst the bottom was the same as built by Dralle twenty-seven years before. The furnace was melting green bottle glass worked out by hand.

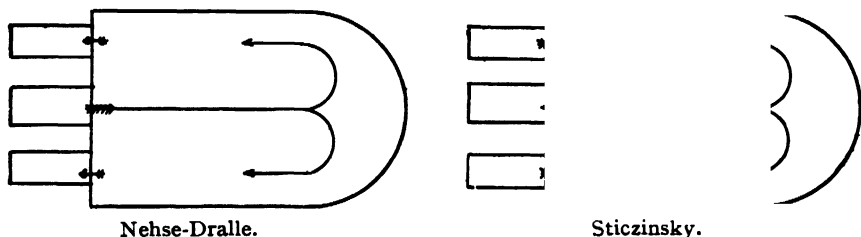


FIG 147.—THE "DRALLE" AND "STICZINSKY" FIRING SYSTEMS.

More modern recuperative furnaces are constructed either with the horseshoe flame or on the cross-flame system. When designed on correct lines and with a suitable and efficient recuperator they can be just as efficient as any regenerative furnace, both as regards output and fuel economy. Such furnaces can have the producers built in conjunction with the tank, or for larger units it may be advisable to use separate producers. In either case the gas is not usually preheated, and care should be taken to place the producer sufficiently near to the tank and to insulate the gas mains.

As an example we refer to Fig. 148, showing a double horseshoe recuperative flame tank designed by Th. Teisen. This furnace has, as will be seen, two step grate producers built in conjunction with the tank and the recuperators. Between the producer and the tank is arranged a dust pocket.

There are two burners in each side on the Sticzinsky principle and the draw-off is in the centre, where the hot gases pass off to each recuperator. The horseshoe flame is not usually favoured with the regenerative type, as the heat distribution is not so good as can be desired. It suits the continuous type, however, and such furnaces are working with good results in many works. The output can be considerably increased compared with what it was in the old "Nehse-Dralle" furnaces. Such furnaces are often supplied with one or two floating bridges and may be used for either hand work or machines.

(283A) **The "Teisen" Recuperative Tank.**—Fig. 149 illustrates a modern recuperative furnace, Teisen's design, with side burners on the cross-flame principle. The tank is supplied with gas from a separate producer, and it will be noticed how simple the arrangement of gas mains is. This furnace is specially designed for machine work, and is supplied with dog

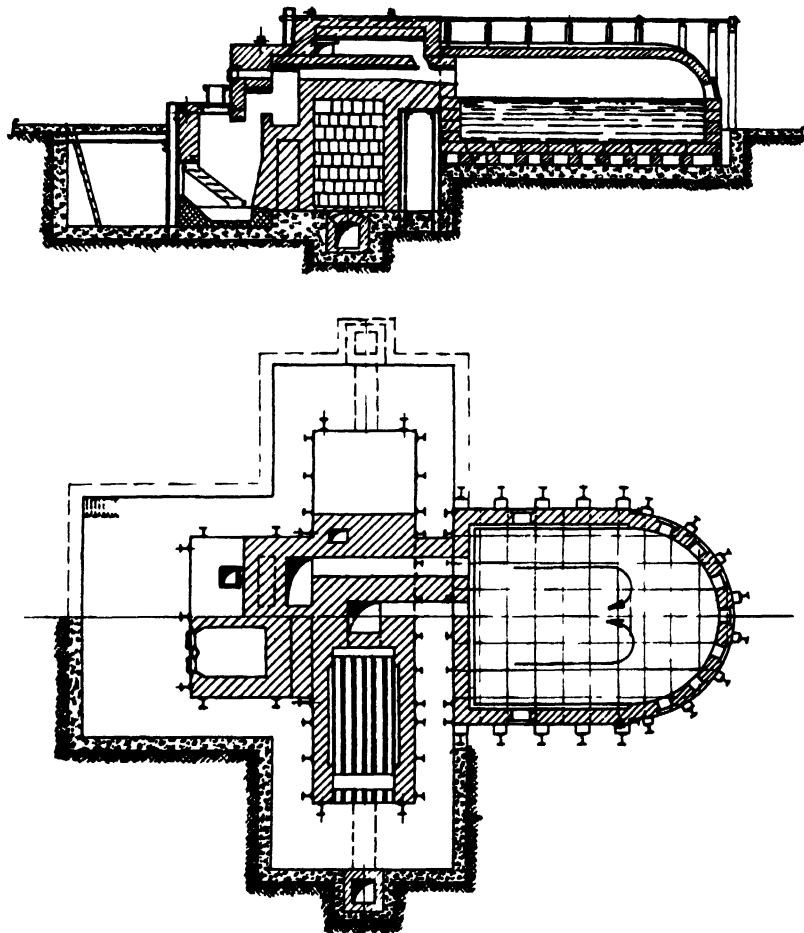


FIG 148.—A "TEISEN" RECUPERATIVE TANK FURNACE (DOUBLE HORSE-SHOE TYPE)

(By courtesy of Th. Teisen, Esq, B.Sc., C.E., Birmingham.)

house and fixed bridge. The flame enters from two burners on either side near the working end. Besides these outlets there are very often one or two smaller subsidiary outlets near the place where the glass is discharged. The recuperators are arranged below, usually in a number of chambers, so that any of them can be shut off for inspection and cleaning without interfering with the rest.

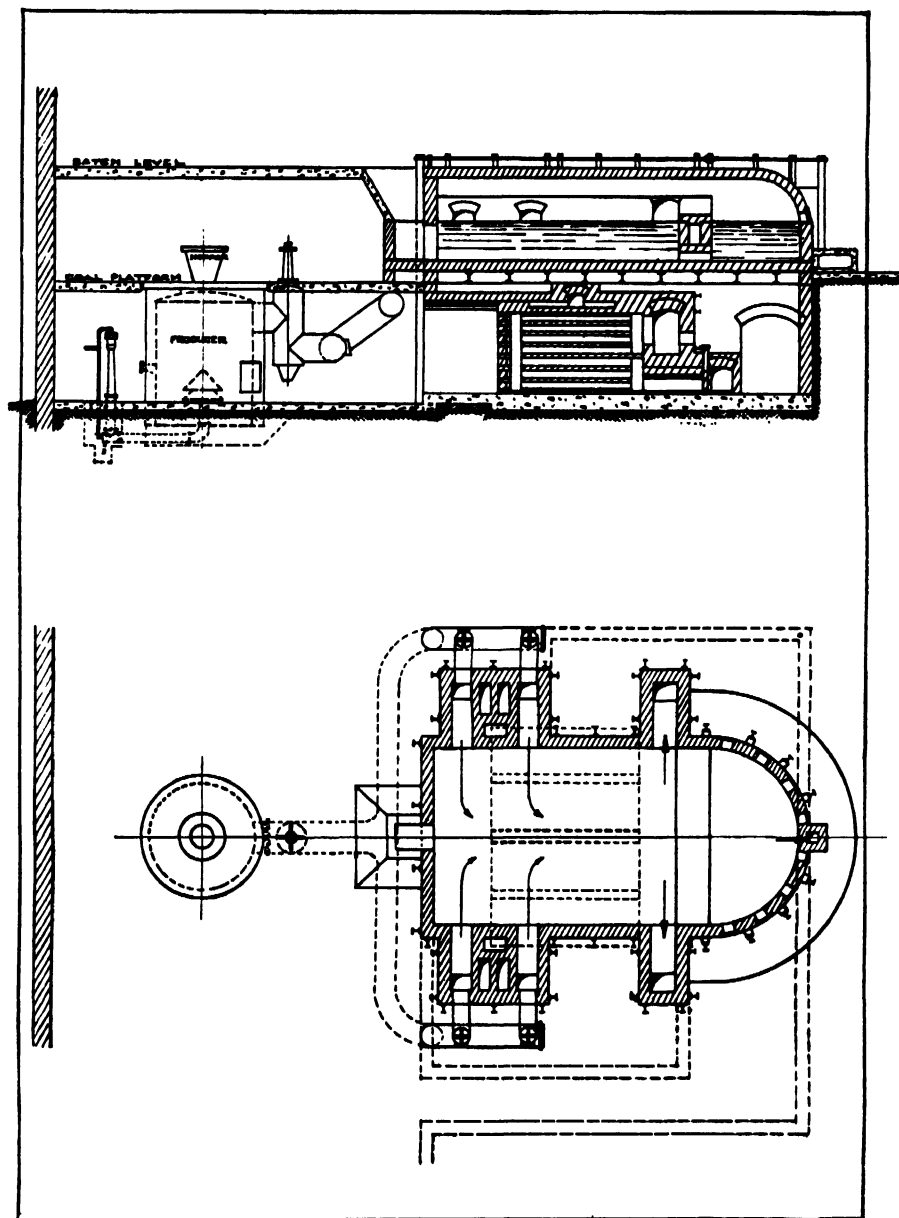


FIG. 149.—A "TEISEN" RECUPERATIVE TANK FURNACE (MODERN CROSS-FLAME TYPE.)

(By courtesy of Th. Teisen, Esq., B.Sc., C.E., Birmingham.)

Instead of the fixed bridge shown, one or two floating bridges might be used. These latter are generally more used on the continent: they require rather more work in setting, but it appears that the life of tanks supplied with these is longer than with the fixed bridge, on account of the action of the glass following other flow lines than in furnaces with a fixed bridge. No doubt the single opening in the fixed bridge has something to do with the wear and tear at that point.

(284) **The "Stein" Recuperative Tank.**—A small recuperative tank furnace (10 feet by 6 feet) designed by Messrs. Stein and Atkinson, Ltd., is shown in Fig. 150. The design of this tank, with "Stein" patent recuperators, is eminently suitable for work with small outputs, and is also an excellent proposition where flint glass is to be worked in a tank. The flow of air, gas, and chimney gases is clearly marked.

(285) **A Comparison of the Regenerative and Recuperative Systems.**—The relative merits of the two recovery systems have long been disputed. Both systems are largely in use in glass-furnace practice, and it is possible by either means to obtain high temperatures very efficiently. The following points are noteworthy in this connection:

(1) The recuperative system occupies less space, and is generally cheaper to instal.

(2) Recuperators are usually used for preheating the air, and in this case it is advisable to have the producers near to the furnace proper to avoid loss of heat. This may be objectionable unless adequate safeguards are provided to prevent entry of dust and soot into the furnace with the gas.

(3) The recuperative system is continuous.

(4) No reversal valves are necessary in the recuperative system and the furnace temperature may be kept more regular.

(5) With the regenerative system reversals, with temperature fluctuations, are inevitable.

(6) Cool gas, from which soot, tar and dust are removed, can be used in the regenerative system, and the producers can be so situated as to suit almost any positional requirements.

(7) The regenerative system avoids dependence upon blocks of high thermal conductivity and somewhat complicated shape and structure. Again, with recuperative heating, difficulty has been experienced in making the brick or tile passages gas-tight and preventing leakage inwards or outwards.

(8) A further difficulty with the recuperative system is that by this method the gas enters the recuperator at a comparatively low temperature, and, since it is not rapidly raised to a high temperature as in the regenerative system, dissociation of the carbon monoxide may occur, reducing the heating value of the gas and tending to choke the recuperator with soot deposit.

(286) **Revolving Pot Furnaces.**—For the automatic machine of the Owens type the glass for working is delivered into a pot or basin. As the machine revolves in a clockwise direction the pot or basin revolves at a higher speed in an anti-clockwise direction. These pots are fitted to one end of a continuous tank furnace, and Fig. 151 shows a revolving pot furnace of the gas-fired regenerative type for this purpose built by Messrs. Simon Carves, Ltd.

The E. W. Harvey Co., Ltd., also construct revolving pot furnaces similar to the above.

A revolving pot furnace of the recuperative type has been patented by J. S. Atkinson and T. C. Moorshead.* A gas and/or air recuperator, 7

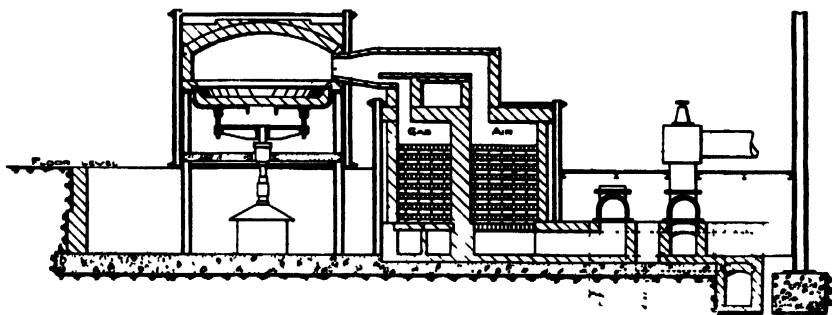


FIG. 151.—A "SIMON-CARVES" REVOLVING POT FURNACE (REGENERATIVE).

(Fig. 152), is employed, in which the waste products flow horizontally to the outlet chamber, 21, and the air or gas to be heated flows vertically without change of direction. As shown, air flows upwards through the

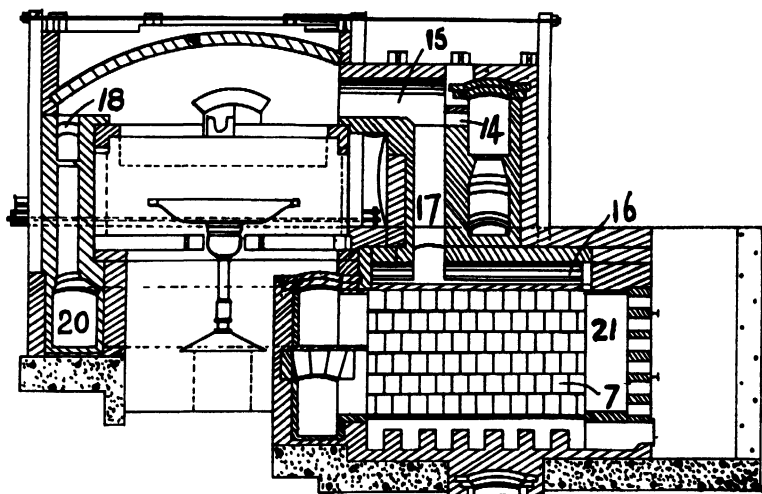


FIG. 152.—A RECUPERATIVE REVOLVING POT FURNACE.

recuperator to the chamber, 16, and thence by flues, 17, to the passages, 15, where it meets gas from the ports, 14. The flames, etc., flow direct to the outlets, 18, which are either in the opposite or the adjacent wall, and thence by flue, 20, to the recuperator.

* *Brit. Pat.*, October 11, 1919, No. 141, 617.

CHAPTER XXVIII

OIL-FIRED FURNACES

(287) **Burners for Oil Firing.**—Oil has been in use for firing glass tank furnaces in this country for at least twenty years. The furnaces so fired are generally of a small capacity, up to about 20 tons, but within recent years tanks of much greater capacity have been converted from producer gas to oil-firing by introducing oil burners in the original gas ports or into specially prepared openings. The small type of furnace is usually of the end-port type with 1 to 4 burners, whilst the larger furnaces are of the cross-flame type with up to 10 burners a side, each side being used alternately. So far as we know, there is no tank or pot furnace operating in this country which has been specially designed for oil-firing. All of those in such use have been adapted for the purpose.

The principle of burning all oil fuel is to break up the oil into drops as completely as possible. This procedure increases the surface very considerably in relation to the bulk of the oil. The effect may be obtained by a variety of methods, and there has been a very great number of burners designed at one time or another. Although in detail each differs from the other, the various systems may be classified under three general headings, thus:

- (a) Steam-injection burners.
- (b) Air-injection burners.
- (c) Mechanical burners.

One of the earliest forms of burner used in this country made use of steam under pressure to break up the oil into fine particles and inject it in that form into the fire-box. Amongst other objections to the system of atomising by steam is the fact that steam is not in itself a combustible substance, nor will it support combustion. If we suppose that the steam is itself decomposed to the gases hydrogen and oxygen, these gases would of course then play their part as combustibles, but it must be borne in mind that the amount of heat required in order to decompose the steam would be approximately equal to that given out by the combustion of the resulting carbon and hydrogen.

Further, the fact that steam does not support combustion prevents the burning of oil taking place as rapidly as it otherwise would. There is, therefore, more chance of unburnt material escaping up the chimney and being lost, and more space is required in the fire-box to complete the combustion.

Although it is a recognised, and hitherto unexplained, fact that steam

has a greater power of atomising oil than has air, the latter is nevertheless more efficient in furnace practice. By atomising with hot air the combustion is far more rapid and more local, therefore the temperature produced is considerably higher. Of course, providing the oil is completely burned, its maximum heat value will be given out, but the local temperature produced will depend to a great extent on the rapidity with which it is brought about. For the purpose of firing melting and heating furnaces the system of hot-air injection is to be preferred for this reason.

All the well-known types of burner running on any one of the three systems can be relied upon to give a satisfactory disintegration to the oil, and the choice of the one system or the other is largely based upon other considerations. Although the atomisation should be as perfect as possible, attention to other details of the installation and the arrangement of the furnace are equally essential for obtaining the best results with the greatest economy when using oil fuel.

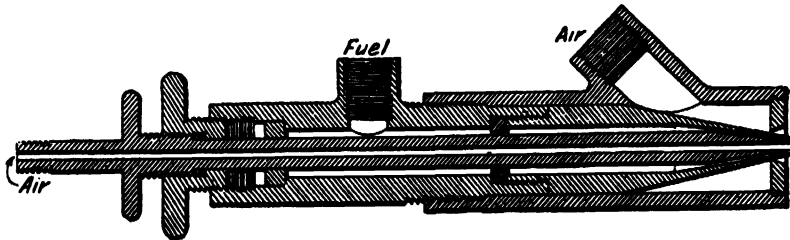


FIG. 153.—THE "CARBOGEN" BURNER.

(By courtesy of the Anglo-American Oil Co., Ltd., London)

From the point of view of simplicity, atomisation by steam takes the first place. The difference in cost and space occupied, as between the system of air injection and pressure injection, is not considerable, but on the score of economy the system of mechanical atomisation heads the list. A burner working on the pressure jet system is capable of spraying considerably more oil in the same time than can be done by either of the other methods, this being especially advantageous when used, as is often the case, in conjunction with forced draught.

Generally speaking, the amount of air required for complete combustion of fuel oil theoretically amounts to about 14 pounds per pound of oil. With a good system of atomisation and of arrangement in the fire-box, 25 per cent. of air in excess of the theoretical requirements should prove quite sufficient, more than this tending to lower the efficiency.

The burner shown in Fig. 153 is the invention of S. F. Stackard, and is supplied by Messrs. J. A. Curle, Ltd., London, who devised the burner for their own particular requirements and find it in every way very satisfactory.

The furnace illustrated in Fig. 154 is of about 6 tons capacity, and the working temperature about 1370°C. ; the view shows the firing end of the furnace and burners which have been in constant use for upwards of two years. In some annealing furnaces to which the "Carbogen" burner

has been applied, the combustion is so absolutely smokeless that no smoke stack or outlet other than from the ordinary openings of the furnace is provided.

According to Brame,* 8 cubic feet of free air per minute are required at 18 pounds pressure to spray one gallon of oil using this burner in glass furnaces.

Other burners have been used on glass furnaces, some complicated and others very simple in design. Burners of the well-known Alldays Kermode, Korting, White, Holden, and Brett types may all be used. Occasionally a burner giving an oil drip in front of an air blast will give very efficient results and is very easy to construct, fit, and replace.

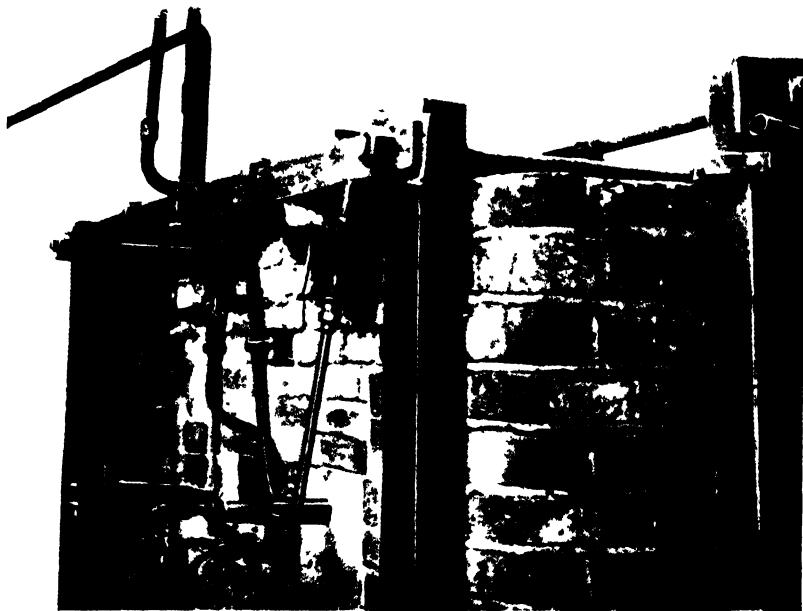


FIG. 154.—AN OIL-FIRED TANK FURNACE.

(By courtesy of the Anglo-American Oil Co., Ltd., London)

W. J. Jones† has described a high-pressure burner for fuel consisting of 50 per cent. creosote and 50 per cent. pitch. The fuel was kept in storage tanks heated to 100° F. by steam coils. Storage tanks 10 feet above the burner and air under a pressure of 60 pounds were used. Oil was introduced by means of a drip feed. An accumulator was resorted to in order to pass air through the burner, thus atomising the oil. On the front of the burner an annulus, into which air was admitted at the same pressure (60 pounds). Around the face of the burner were serrations through which the air was passed in a "solid" ring, so as to prevent the atomised oil from spreading too quickly. With this burner a narrow stream of atomised oil and high-pressure gas passed well into the

* *Fuel*, Arnold, 1920, p. 132.

† *Pottery Gazette*, 1920, 45, 767.

furnace. The results were so efficient that with a single burner of this type a furnace 15 by 8 feet containing 8 glass pots could be kept at a constant flame temperature of 1500°C . The oil consumed was about 16.8 gallons per hour.

J. Connolly* has given details of a large oil-fired tank using kermode burners, operated for several years, working 8 holes continuously night and day, and considered it a very satisfactory proposition. The oil was injected under a heated air pressure of 10 pounds per square inch. It was essential to see that the burners were regularly cleaned, as carbon was deposited on the nose. The Anglo-American Oil Co., Ltd., have, a short time ago, carried out experiments with regard to the oil-firing of glass furnaces, more particularly those of the crib furnace type using skittle pots, as the oil-firing of these furnaces had not been hitherto successfully carried out.

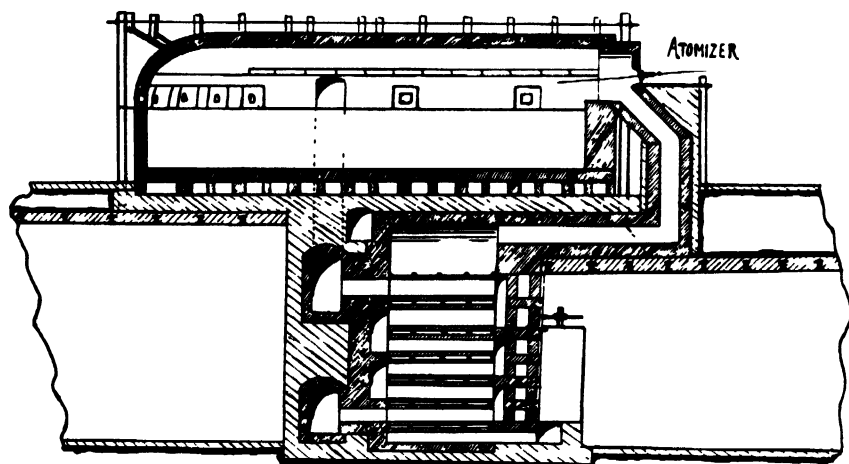


FIG. 155.—AN OIL-FIRED TANK FURNACE WITH RECUPERATION.

The furnaces, which had previously used coke as fuel, were converted to oil-firing by closing up the bottom and placing an Allday's No. 3 burner at one side so that the flame projected right across the furnace to the other side. The air pressure used was from $2\frac{1}{2}$ inches to 4 inches of water, and very satisfactory results were obtained, the consumption of oil being about $3\frac{1}{2}$ to 4 gallons per hour. The furnace contained 4 pots, each holding approximately $4\frac{1}{2}$ cwt. of glass.

They found that it was possible to melt from batch in these pots, but the proposition was not so easy as when making from cullet, since the founding heat required for batch melting is so much higher than the heat required for working from cullet. The glass which was being worked out from one pot ran off the blow-pipe if the heat of the furnace was kept up to founding heat for another pot, and if the heat was reduced to enable the glass to be worked it was then insufficient to found the batch which was lying in a second pot. This difficulty could be overcome

* *J. Soc. Glass Tech.*, 1921, 5, 291.

by blowing air into the particular pot which was being worked out. It was found that the life of the pots was somewhat longer than when coke was used, due to the heat being constant instead of fluctuating with the recharging of the furnace with solid fuel.

Oil-firing for glass furnaces is, therefore, in certain cases, a really practical proposition. Local heating and the resulting cracking of pots has prevented its use, except occasionally, for pot furnaces. Recuperation or regeneration of the secondary air is essential for good and efficient working, and, generally speaking, the crown of an oil-fired furnace should be lower than in the gas-fired type. Providing the oil is warm, the secondary air hot, the regulation of oil and air correct and atomising complete, oil-firing is really efficient.

A tank furnace designed for oil-firing, with recuperative preheating of the secondary air, is illustrated in Fig. 155.* With regenerative preheating of the air it is necessary to have the burners so arranged that they can be removed from the exit ports when the flow of gases is reversed.

Whether or not a manufacturer will find the over-all cost of oil furnaces cheaper or more expensive than producer-fired furnaces depends ultimately upon the possibility of a constant supply of oil and on its price.

* *Sprecksahl*, 1922, 55, 4.

CHAPTER XXIX

POT-ARCHES AND GLORY-HOLES

(288) **Direct-Fired Pot-Arches.**—Pot-arches, the furnaces in which the pots are very slowly heated before they are put into the melting furnace, require an efficient regulation of temperature to be a real success. It is curious that in past years, in many works, the most primitive heating methods have been used in this connection. There may be seen, even at the present time, brick chambers in which the pot is placed surrounded by fires, the only means of temperature regulation being the skill of the man attending to the fires and a simple chimney damper in the roof of the chamber or kiln. Whatever success is attained in the heating of pots by this method is a direct tribute to the furnace man's care and skilful supervision. At the present time such methods cannot hope to be sufficiently safe to compete in practice with modern methods of pot-arching.

The ordinary old style pot-arch (see Fig. 156) usually had a fire-box on either side of the door in front, arranged about midway between floor and crown, with an outlet for the burnt gases in the back wall near the bottom.

This arrangement is bound to give certain cold pockets in the inside of the furnace. When heated up slowly, the lack of proper heat distribution can be somewhat counteracted, since sufficiently long soaking has a tendency to produce a uniform distribution of the heat.

The temperature to which such a pot-arch can be raised is usually very moderate, especially where high-class fuel is not obtainable.

The usual manner of operating this type of pot-arch is to start with a small fire, leaving plenty of smoke in the arch for a number of days. During the last few days the temperature is increased to the neighbourhood of 1000°C . and the pots set in the furnace, the temperature of which is also rather low.

The increasing use of the gas-fired pot furnace in the glass industry called for a more modern type of arch, in which the heat distribution would be more uniform and under better control, and where the temperature obtainable would be higher, at least 1200° to 1300°C .

Bleining* urged "that the construction of pot-arches be changed to a type making possible more uniform temperature distribution, as well as higher temperature. The down or up draft kilns with perforated bottoms, used extensively in the clay industries, were recommended. The

* *U.S. Bureau of Standards, Tech. Paper No. 144, 1920, p. 52.*

rate of heating the pot-arches should conform to the critical temperature ranges applying to clay—viz., the expulsion of the hygroscopic and of the combined water and the oxidation of carbon. Halts should be made within these ranges until the changes involved are completed. Between and beyond the critical temperatures the heating may be more rapid than prescribed by the present practice."

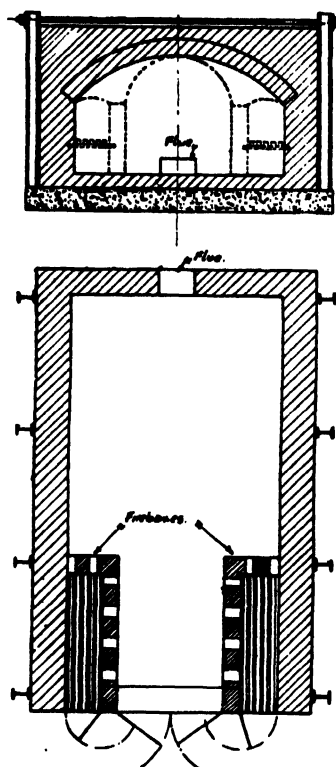


FIG. 156.—AN OLD STYLE POT-ARCH
(By courtesy of Th. Teisen, Esq., B.Sc., C.E., Birmingham.)

The furnace type which these remarks foreshadowed has already been anticipated in this country by the "Teisen" semi-gas-fired recuperative pot-arch, the first of which was built in 1917 by the Edinburgh and Leith Flint Glass Co., Ltd., and this type will be described later.

(289) **Gas-Fired Pot-Arches.**—A pot-arch heated by producer gas is shown in Fig. 157. The main gas-flue **A** passes in front of the arch and the gas is led off through a water-sealed, cast-iron pipe **B** provided with a valve, into a flue extending under the floor of the arch. Secondary air enters by a flue **D** below the gas and is thus somewhat preheated. Gas and air mix at **E**, pass up into the arch, so giving a well-spread flame. Exit ports lie in the front of the chamber near the bottom, on each side of the door.

Fig. 158 shows a semi-gas-fired recuperative pot-arch (Teisen's design), worked on the down draught principle, with the producer at the back of the chamber. The gases enter the furnace through a "parallel"

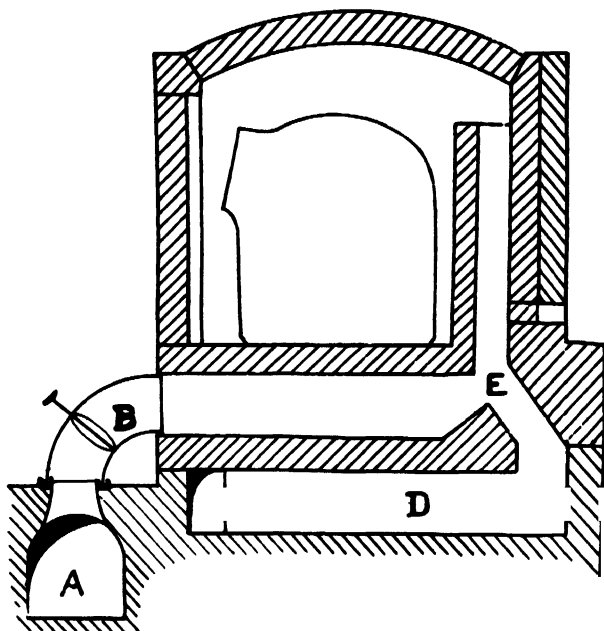


FIG. 157.—A GAS-FIRED POT-ARCH.

burner, where intermixing takes place, and consequently the combustion first occurs in the chamber itself, with the result that the flames fill the arch, completely enveloping the pots.

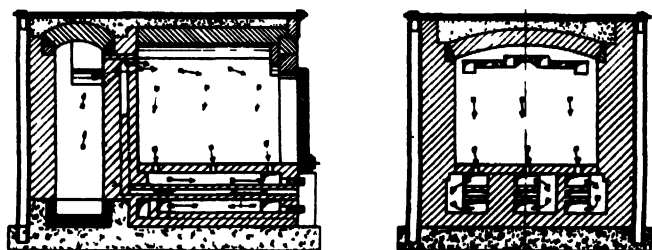


FIG. 158.—TEISEN'S GAS-FIRED RECUPERATIVE POT-ARCH.
(By courtesy of Th. Teisen, Esq., B.Sc., C.E., Birmingham.)

The burning gases are drawn down through holes distributed over the floor and under the pots, which are placed in the usual manner on bricks, so that the burning gases actually sweep the bottoms of the pots.

Under the floor tiles is arranged the recuperator, which consists of a number of straight air channels, covered above and below by waste gas channels. The feature of this arrangement is its simplicity, and care has been taken to insure that no leakage occurs due to the alternate heating up and cooling down. Pot-arches of this special design are stated to have been working four or five years, heated up once or twice a month, without any trouble or leakage.

During the first stage of burning a low fire, fed through the ash door, is kept burning on the grate. Water, dripping on the bars, produces a certain amount of steam.

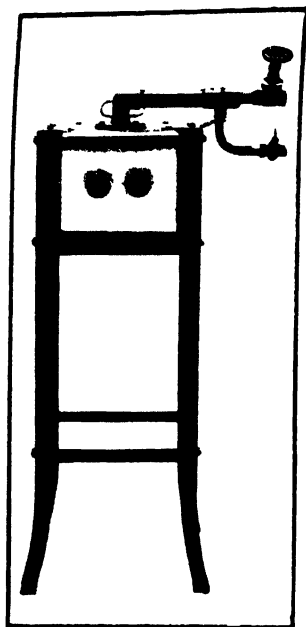
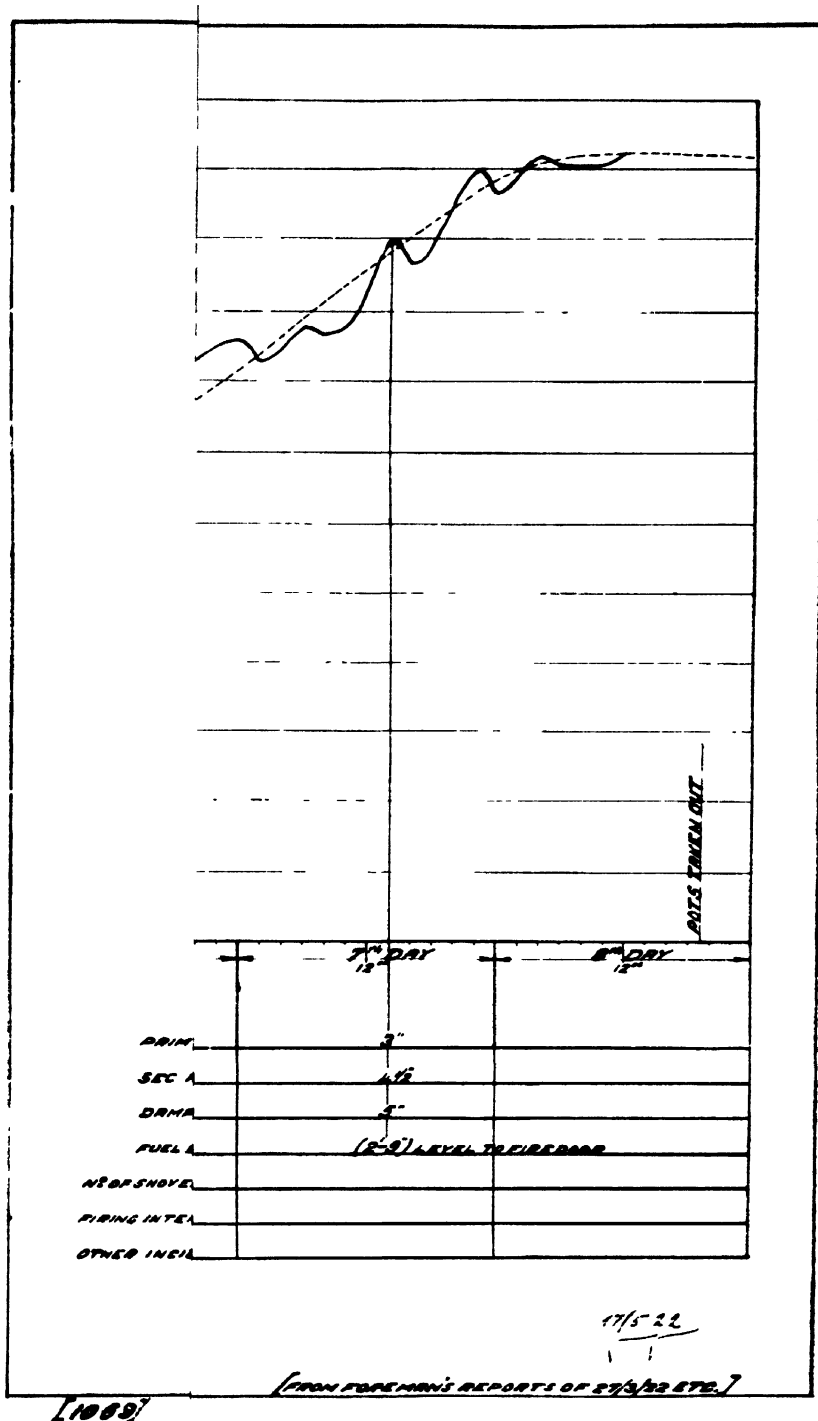


FIG. 160.—GAS-HEATED GLORY-HOLES.

(By courtesy of the British Commercial Gas Association, London.)

The secondary air inlet is closed, and the furnace is thus direct-fired at this early stage. It is not necessary to run the furnace so full of smoke as is the old practice, since steam will have the same effect as smoke of retarding the drying of the outside of the pots. It is a matter of driving out the natural and later on the combined moisture, and that can only be done from the inside of the clay wall, by heating the pots up slowly. The pots, in other words, "sweat" the moisture out. As the heating proceeds the fuel layer is slightly increased, and some secondary air is usually admitted in the producer; at this stage the furnace is semi-gas-fired.

When the furnace is dull red, secondary air from the recuperator can be admitted and the fuel-bed slowly increased until it works as a fully



gas-fired furnace. It is now fired through a door arranged about 3 feet above the grate level. This stage in the operation is commenced when the hygroscopic moisture is expelled.

A curve is reproduced in Fig. 159 showing the rate of heating up of a pot-arch of this type. It should be remarked the temperatures registered are not true temperatures, the maximum temperature being approximately 1250°C . On account of an opening near the pyrometer the curve was not quite as regular as it otherwise might have been. Temperatures up to 1350°C . have been obtained in arches of this design. The producer shown, instead of being level with the floor, might be arranged below, in which case a still better heat distribution would possibly be obtained.

(290) **Glory-Holes.**—Glory-holes are used for reheating glassware evenly in a very short time preparatory to shaping with tools, etc. They may be fired with coal-gas, oil, or producer gas.

The simplest form consists of a rectangular fireclay box, made either of bricks or slabs. The interior measures about twelve inches in length by six to nine inches in width and the same in height. In each side is a hole into which the ware is inserted for reheating; one apparatus therefore serves for two sets of workmen. Through an opening in one end of the chamber oil or gas and compressed air are blown, their combustion giving the desired heat. Heavy oil appears to be rather unsuitable for use in glory-holes, since large carbon deposits form on the burners. Crude creosote or tar-oil is generally used. Burners employing compressed air, and oil warmed by steam coils, give a full, "fat" flame which heats more rapidly than a gas flame.

Fig. 160 shows a glory-hole, designed by B. W. Brooks, which is heated by coal-gas. The coal-gas-heated glory-hole is clean, easily regulated, takes up little space, is cheap to instal, and does away with fuel storage.

CHAPTER XXX

ANNEALING FURNACES

(291) **Kilns.**—The principles of annealing have already been dealt with in a previous chapter. In commercial practice two chief types of furnace are used for annealing—namely, the kiln and the continuous annealing furnace called the “lehr.”

The kiln usually consists of a brick chamber with a single or double door according to the size of the kiln. An opening is made in the door of a size convenient for the introduction of the glass articles. Two small openings are made at the bottom of the side walls near the door, and a third near the roof at the back of the kiln.

A coal or coke fire is started near the door, deriving air from outside through the holes in the side walls. This fire is maintained until the whole chamber is uniformly heated to the annealing temperature, by which time the fire frequently reaches the level of the bottom of the opening in the door and shelves gently down to the floor of the kiln. All crevices are clayed over, only the draught holes and the hole in the door remaining uncovered. The latter may be covered by an iron plate during such time as glassware is not being put into the kiln. Waste gases find exit by a dampered flue over the door.

As the articles are made they are piled in the chamber until it is full. The door opening is closed and the temperature reduced by time limits until the kiln is cool enough to be opened. The door is opened slightly at first, then a little wider, and finally the opening at the back of the kiln is uncovered.

Skilfully and scientifically accomplished, kiln annealing is a very effective mode of procedure; almost perfect annealing can be obtained. It is, however, a very slow and uneconomical process, and is now almost entirely confined to heavy glassware for table use and similar articles on which work, such as cutting and engraving, has to be done subsequently. In America, gas-fired muffle kilns are used for thick glass jugs, tumblers, etc.

(292) **Pan or Continuous Belt Lehrs.**—For the majority of types of glassware, the kiln has been superseded by the pan, or continuous belt lehr. In the ordinary pan lehr, as originally designed, an attempt has been made to duplicate the conditions prevailing in kiln annealing. The glass articles are placed upon pans in the end of a tunnel, this end being heated by open fires of coal or coke, or by gas burners. By this means a gradually falling temperature is obtained along the tunnel. As one pan becomes full, another is pushed into the tunnel, and so the pans

slowly pass out of the heated zone, cooling gradually as the other end is approached. It is necessary to allow free access of air at the entrance of the lehr in order that the fires shall burn. Consequently draughts develop in the lehr which cannot be other than inimical to good annealing. Little control of temperature is usually attempted, and the rate of cooling down the tunnel, only controlled by chimney dampers on the lehr, is very unsatisfactory and a matter of guesswork. The fuel costs are out of proportion to the amount of heat required. Lehrs of this type with sundry improvements are largely in use at the present time, and meet with a very fair measure of success where reasonable care is taken.

The fore-part of the lehr usually consists of a firebrick combustion chamber of a length about 10 to 15 feet, and this leads into a tunnel, from 5 to 12 feet in width, the total length varying from 35 to about 100 feet in ordinary cases. For window glass and plate-glass, annealing lehrs of 300 feet or more in length are used. Lehrs are usually gas-fired, though oil, coal, or coke are still used.

The combustion chamber should be so constructed that the temperature attained by the ware, and the length of time during which this temperature is maintained, are sufficient to ensure that all strain is removed from the articles. The tunnel should be of such a length and have such a temperature gradient that the ware from the combustion chamber is cooled and taken from the lehr as quickly as possible without the reintroduction of strain.

The carrying arrangements may consist of pans linked one to another or a continuous belt, mechanically driven, and the speed regulated according to the size and nature of the ware.

The introduction of chain-screens at the mouth of the lehr prevents draughts and assists proper operation of the lehr.

Modern lehrs vary in design quite as much as furnaces, but those described in succeeding pages are typical of the best present practice.

Now, in the ordinary lehr the flames rise towards the top of the crown, and pass along the lehr towards the chimney outlet or outlets arranged in the top of the crown some suitable distance from the discharging end. The gases, on account of being lighter than the air, are drawn upwards, and actually move just beneath the arch all the way. Under the pans or belt there is usually a waste space into which a false air current enters, and which cannot be reached by the hot gases. Consequently, such lehrs are often found to be too cold on the belt or pan level, and the difference in the temperatures at this level and the top is quite considerable. Further, while the temperature gradient just under the crown may be fairly satisfactory, if a similar curve was taken near the belt-line it would be found that this, instead of following the other, would fall much more rapidly, which would have the effect of cooling the bottom of the ware much quicker than desired. In certain ware such as bottles or jars the bottom is actually thicker than the top, and instead of cooling the bottom at a greater rate than the thinner top, it would be better to retard the cooling of this part.

(293) **A "Harvey-Siemens" Lehr.**—The lehr illustrated in Fig. 161 is built by the E. W. Harvey Gas Furnace Co., Ltd. It is designed for heating by gas from the gas producers serving the melting furnace or

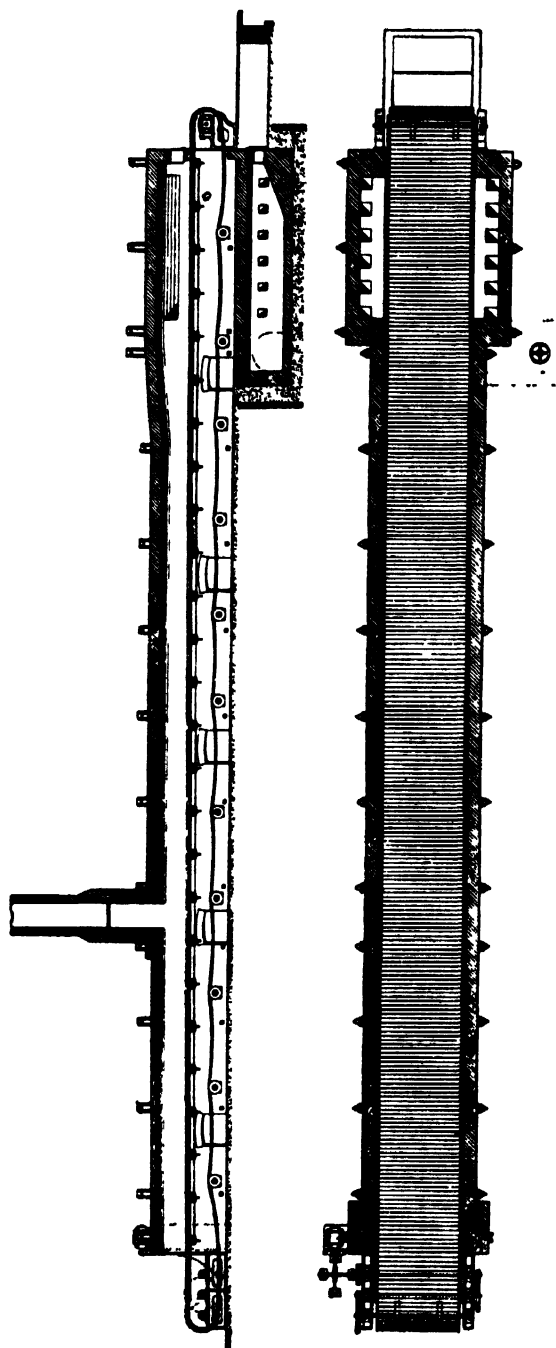
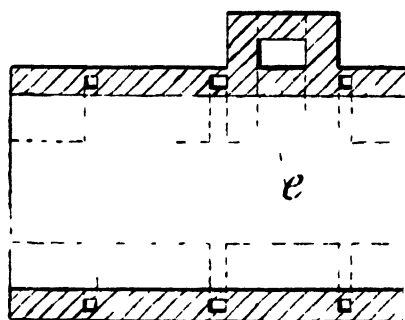
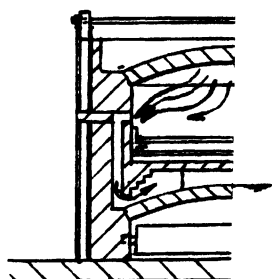
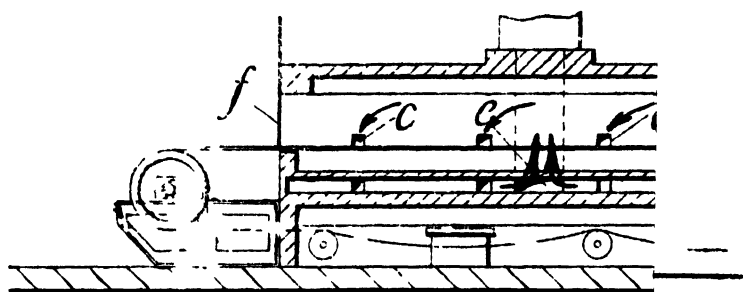


FIG 161 —A "HARVEY SIEMENS" LEHR
(By courtesy of the E. W. Harvey Gas Furnace Co., Ltd., London)



from a small separate producer, and is primarily intended for the annealing of bottles.

The bottles coming from the machines are placed on the endless travelling belt at the hot end of the lehr, which is heated by a gas flame of regular length and quality, issuing from a series of ports on either side; thence the bottles travel through a longer portion of the lehr, which is kept warm by the products of combustion from the gas flame, but always with a gradually decreasing temperature, until the bottles arrive near the discharging end of the lehr cool enough to be taken off the travelling belt and placed on trucks, etc., ready for washing and warehousing.

For inducing the gas flame and products of combustion to travel regularly along the lehr towards the cool end, a small chimney is erected in a suitable position, its draught being regulated by a damper easily adjusted as desired.

The travelling belt runs on several rows of rollers, or wheels, and is guided between angle irons to keep it straight. The belt is driven by a small variable-speed electric motor operating through efficient worm and worm-wheel speed-reduction gear, whereby the belt travels at the rate of 8 to 16 feet per hour.

A hand-power reduction gear can be fitted, which may be used at once should the electric power fail.

The patent driving chains, in which the steel laths forming the belt are fastened, are of the best malleable cast iron, and any "slackness" of the chains can be taken up by a good tightening gear provided at one end of the lehr.*

(294) **The "Teisen" Lehr.**—In the "Teisen" gas-fired lehr the keynote of the whole design is the application of bottom heat both to the heating chamber as well as to the cooling chamber. By this means is obtained a more uniform temperature over any cross-section of the lehr, together with a suitable temperature gradient along the length of the lehr.

Fig. 162 shows sufficiently clearly the principle of the design. The lehr is heated by a step grate producer arranged below the heating chamber. It can also be heated by gas from a separate producer, or in any other manner. A combustion chamber is arranged in each side wall of the heating chamber, and the flames emerging from the burner openings are distributed all over the vault in broad, thin bands of fire. Each burner can be kept under control, and the temperature in the front end can thus be varied to suit the glass charged. The bottom of the lehr under the heating chamber is intersected by heating flues communicating with the combustion chambers, and impart heat to this part of the brickwork, which again radiates it to the belt from below. Both the sides and bottom of the heating chamber act in this furnace as a muffle, imparting heat by radiation, and by their mass help considerably to keep the temperature steady inside the chamber.

The burning gases are drawn away towards the cooling chamber, in the bottom of which are arranged one or two longitudinal flues (d) communicating with the chamber through ducts (c) which are arranged

* The principle is also applied to muffle lehrs.

below or near the level of the pans or belt, and distributed all along the length of the chamber. The bottom flue, again, has one or more outlets to the chimney. The hot gases passing along the lehr are drawn down towards the belt, as shown in the cross-section, and enter the bottom flue (d), imparting part of their heat to this before going to the chimney. Each "draw-off" can be regulated.

In this manner the temperature difference over the cross-section can be reduced to a minimum.

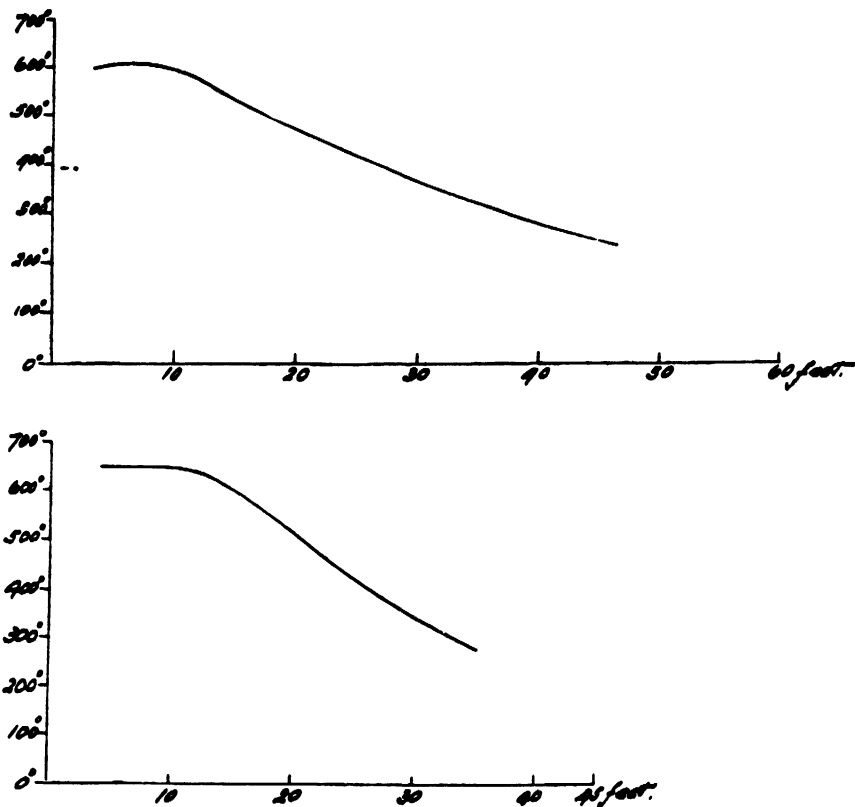


FIG. 163.—CURVES SHOWING COOLING RATES OF TEISEN LEHRS.

(By courtesy of Th. Teisen, Esq., B.Sc., C.E., Birmingham.)

The bottom flue usually extends the length of the arch above, and it is evident that so long as the hot gases are passing along the top, to ensure a good heat distribution over the cross-section, some will have to be drawn down fully or in part to the ducts in the bottom. To prevent making the far end of the bottom too hot, the "draw-offs" are grouped, each group having its own outlet to a separate chimney. Two such chimneys, suitably distributed along the lehr, are usually found sufficient for this purpose. To support the bottom draught and to hinder any cold current, several asbestos curtains are arranged along the length.

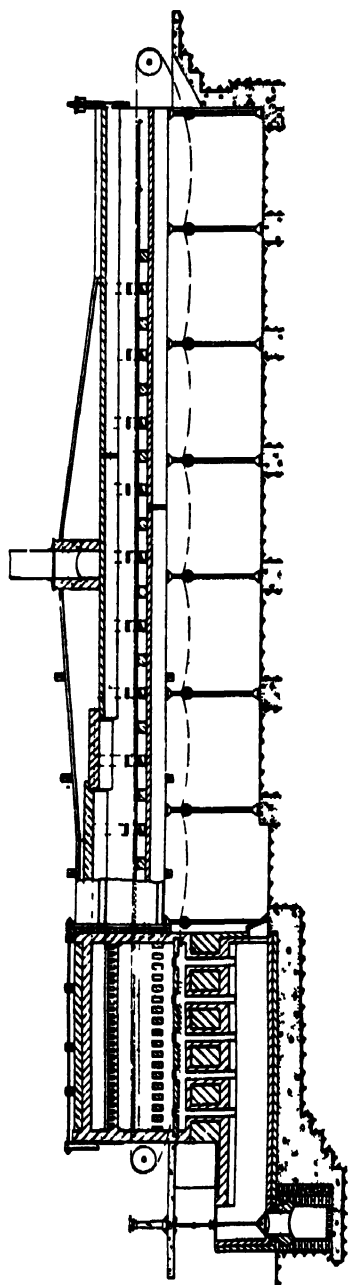


FIG. 164 —A "SIMON-CARVES" LEHR.

(By courtesy of Messrs. Simon-Carves, Ltd., Manchester.)

The goods leave the brick part of the lehr with a temperature sufficiently below the critical one of the glass, and if they need any further cooling for handling, the belt may be prolonged, as the cooling can then be done more quickly than the closed-in brickwork allows.

In this way very satisfactory annealing results have been obtained, and two curves, one from a 60 by 7 foot lehr, and the other from a 45 by 5 foot lehr, working on fairly heavy machine-made jars and bottles, passing through at the rate of $3\frac{1}{2}$ hours, are reproduced in Fig. 163. Both show a very gradual temperature fall along the lehr.

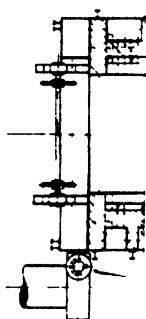
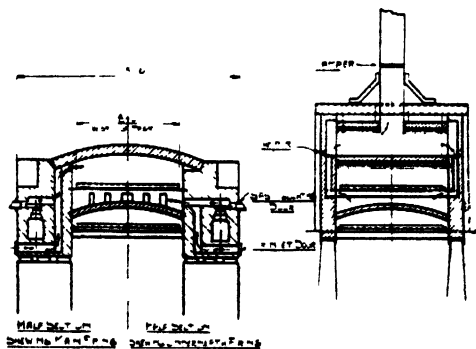
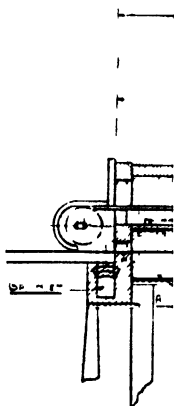
As the output of a lehr is determined by the greatest fall in temperature in a certain time interval, it is evident that the more regular this is, and the nearer it can be made to follow the annealing curve of the glass, the greater the output obtained.

(295) **The "Simon-Carves" Lehr.**—Another lehr, built by Messrs. Simon-Carves, Ltd., is illustrated in Fig. 164. It is a standard type continuous lehr. The lehr tunnel is supported on steel work, and the hot gases from the combustion chamber exhaust downwards between the articles and the slats of the band, and into the space below the band. This space is divided into several compartments, each of which contains an exit flue on either side, these flues passing vertically up the side walls into two collecting squirrel-tail fans connected to the chimney. The chimney is about 40 feet high. The lehr is driven as above by an electric motor, and runs continuously at a few inches per minute according to the output of the automatic machine and the size of the ware.

(296) **The "Stein and Atkinson" Lehr.**—A fourth lehr of the "open" type is shown in Fig. 165, and is built by Messrs. Stein and Atkinson, Ltd. This lehr is fired at the charging end by a series of burners on either side, extending for some distance down the lehr according to the total length of it. The burners or ports are so arranged that they can be independently regulated one from the other, so that the initial temperature of the lehr can be varied to suit all conditions of the annealing of glassware. One port is arranged on either side, just inside the charging end underneath the belt, this arrangement preventing the cracking of the ware due to uneven temperature. The products of combustion, instead of passing over the ware, are drawn down to the underside of the belt, outlets being arranged in the side walls, whence the waste gases pass to the chimney. The "uptakes" leading to the squirrel-tail flues are each provided with a regulating slide, by which means the temperature throughout the length of the annealing chamber can be increased or decreased at will at any point of the lehr. The lehr may be fired by independent gas producers, or a producer can be built adjoining the firing end of the lehr, this producer using either coal or coke as fuel.

(297) **Muffle Lehrs.**—In the average open type of lehr the following disadvantages* are usually found: (1) Glass cannot be satisfactorily annealed owing to the arch being further away from the glassware in the centre of the lehr than at the sides; (2) to obtain sufficient heat to anneal the glass properly in the centre of the lehr, it is often found that the glass at the sides is melted down; (3) glassware from an open type lehr, whether

* C. E. FRAZIER, *National Glass Budget*, 1919-20, 2, 1



Gen. _____
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the lehr is fired by producer gas, oil, or direct coal or coke fires, is always covered by a bloom—i.e., is "sulphured."

The muffle type lehr prevents the bloom being deposited on the glass, since the flame does not come into contact with it.

(298) **The "Simplex" Muffle Lehr.**—The "Simplex" muffle lehr* (see Figs. 166 and 167) is designed with a flat arch supported by cast iron and permitting the use of thin tiles, and, accordingly, increasing radiation and decreasing fuel consumption. The breakage of tiles, generally a considerable item in the circular-arch type of lehr, is reduced to a minimum, since the tiles have only their own weight to support and

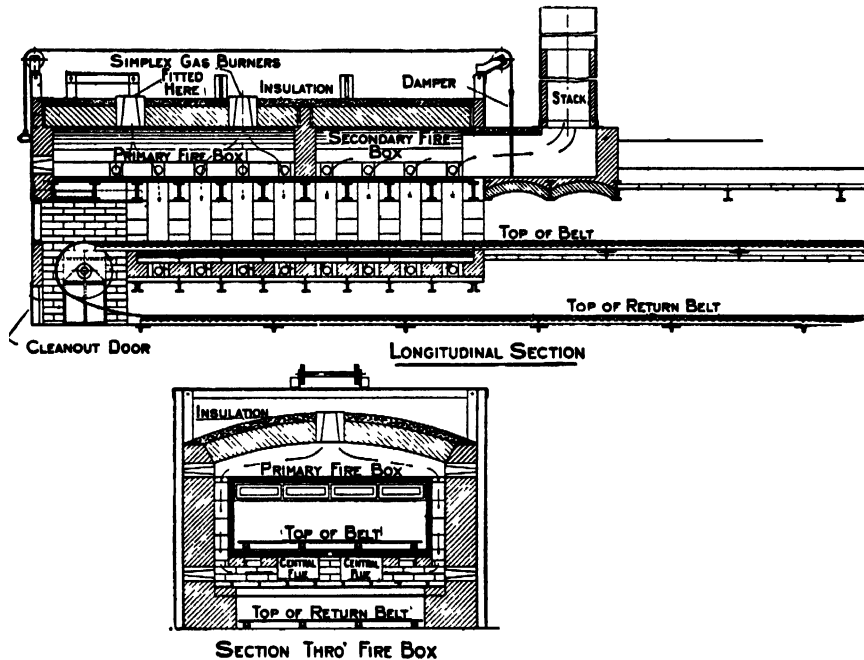


FIG. 166.—THE SIMPLEX MUFFLE LEHR.

(By courtesy of the Record Engineering Co., Ltd., Tutbury, Burton-on-Trent.)

the construction of the lehr is such as to allow free expansion and contraction. Broken or cracked tiles can be replaced through the clean-out doors, whilst the lehr is in operation. The burner, of simple and strong construction, is in the top of the firebox, the flame being drawn down either side and underneath the pans; it is also in an easily accessible position and ensures a self-cleaning fire.

Draught control being applied to each lehr, a uniform temperature is obtained throughout the fire-box, together with an economical distribution of the heat. The system of dampers in the fire-box is so arranged as to permit of transference of heat to wherever it is necessary. The Simplex muffle lehr is stated to have proved that a uniform temperature

* C. E. FRAZIER, *loc. cit.*

throughout the fire-box and a uniform fall of temperature throughout the first 25 feet were essential to the efficient annealing of glassware. The

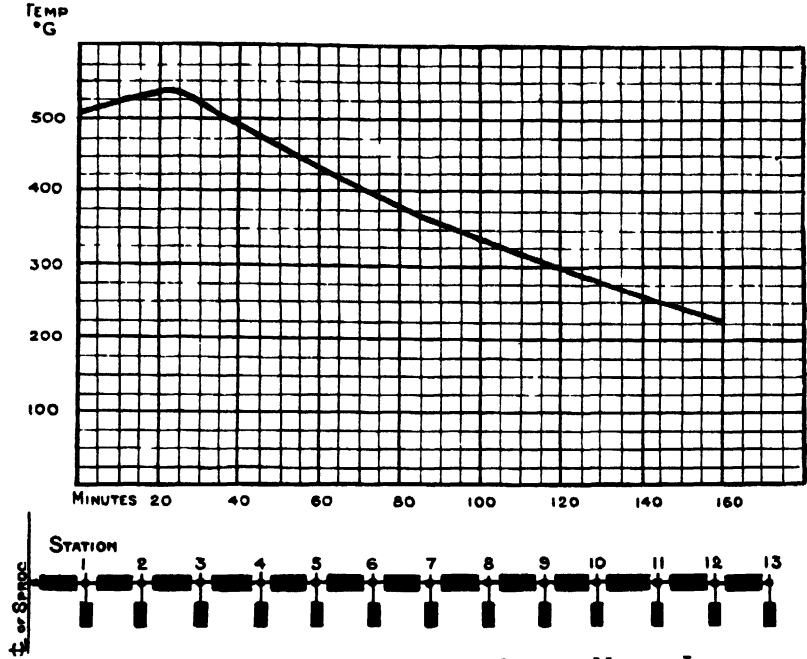


FIG. 167.—TEMPERATURE CHART FROM A SIMPLEX MUFFLE LEHR.
(By courtesy of the Record Engineering Co., Ltd., Tutbury, Burton-on-Trent.)

following figures show the difference in this respect between the open type and the muffle type of lehr:

Distance from Front of Lehr.	Temperature (Degrees C.).	
	Open Lehr.	Simplex Muffle Lehr.
9 feet	900	900
15 "	725	820
20 "	560	760
25 "	525	700
30 "	420	580
35 "	300	440
40 "	220	380

The Simplex muffle can be applied to old lehrs, whether of the hand-pulled or continuous type.

(299) A "Stein and Atkinson" Muffle Lehr.—Fig. 168 shows a muffle lehr with continuous belt designed by Messrs. Stein and Atkinson, Ltd., and the drawing is self-explanatory.

(300) **The Dixon Muffle Lehr.**—The muffle chamber (see Figs. 169 and 170) is made up of ten or more flue units; the first four in front being heated by the initial combustion of gases and the six rear flues utilising the waste heat from the front flues. To provide for wide lehrs, the flue areas are small, increasing the velocity of the gases and increasing the flame length to provide for a uniform temperature over the entire width of the Lehr. In this respect, lehrs up to 20 feet in width will operate equally as well as lehrs only 8 feet wide, and require very little more fuel for the operation. The waste gases passing under the incoming

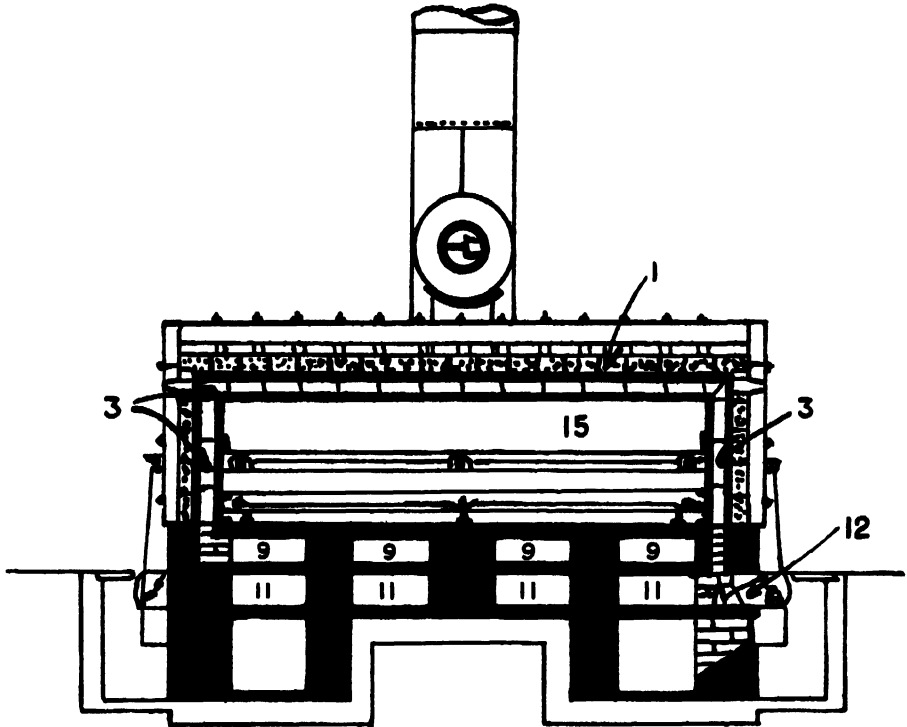


FIG. 170.—THE DIXON MUFFLE LEHR.

(By courtesy of the H. L. Dixon Co. Ltd., Pittsburg, Pa.)

pan ensure a pan temperature high enough to entirely eliminate the bottom checking usually encountered. With the flue arrangement employed, it is possible to regulate the temperature of the muffle chamber every 18 inches of its entire length, which is 15 feet. This duplicates the temperature control which was possible with annealing kilns.

The temperature control of the Dixon muffle is very good in that the actual temperature of the ware is measured within the accuracy of the thermo-couple. This is due to the fact that the atmosphere in the muffle is still, or quiescent, and the ware and muffle are maintained at the same temperature by radiant heat. In the case of the open fire Lehr,

the ware is surrounded by rapidly moving air and gases, which, of necessity, require a high temperature gradient between the moving gases and the ware. In most cases the thermo-couple in open fire lehrs is located in such a position that the flame and hot gases impinge upon it and the temperature of the flame and not the ware is recorded. For this reason it is often necessary to reduce the annealing temperature in the Dixon muffles several degrees lower than was formerly used in open fire lehrs to prevent melting of the ware. Furthermore, a positive pressure is constantly maintained within the entire muffle and lehr chambers, making impossible the entry of any outside air and preventing any currents or objectionable draughts. A quiescent atmospheric condition is therefore maintained within the muffle and lehr chamber, which is even better than that secured with the annealing kiln. At the same time a very slight negative pressure is secured inside the flue, which prevents leakage of gases into the lehr, even though a tile become cracked or broken.

The air for combustion is heated before it reaches the combustion chamber, and can be regulated to the exact amount required for the complete combustion of the gases. The muffle or hot zone of the lehr is completely covered by insulating material, thus reducing the loss by radiation to the minimum.

The lehr, or cooling chamber, is constructed of steel in place of the usual brick construction to facilitate rapid cooling below the critical thermal point, care being taken to insulate a portion of this chamber to insure against damage due to a too sudden drop in the temperature. Waste heat vents provide for the regulation of the cooling chamber to the required temperature; consequently accurate temperature control is possible throughout the entire length of the lehr.

It may be noted that in the ordinary muffle lehr the fuel is introduced through the crown, with the result that no bottom heat is obtained. The Dixon muffle is constructed to secure a maximum of bottom heat without losing temperature control. This will be appreciated more when used as a decorating lehr, where colour must be burned out uniformly top and bottom, and as an annealing lehr for stem ware, fruit jars, and other ware requiring special conditions.

Through several cone tests recently made on 7, 12, and 15 feet wide lehrs, the results were better than expected, showing an absolutely uniform temperature across the entire width and height of the chamber. Annealing tests under the most exacting conditions have been repeatedly made. In one particular instance the annealing time required for a certain class of ware was stated to have been reduced from nineteen to eight hours with a saving of fuel of 25 per cent.

CHAPTER XXXI

THE MANIPULATION OF GLASS

I. Bottle-Making by Hand.

(301) **Introduction** —The method of making bottles by hand is being rapidly replaced by the machine method. However, since hand-working still widely prevails, we propose to describe the two chief modes of operation by hand.



FIG. 171.—BOTTLE-BLOWING (HAND PROCESS).

(By courtesy of Messrs. T. Barron and Sons, Ltd., Mexborough.)

(302) **The Common Bottle Process** (see Fig. 171).—In the making of bottles by this process, the workers combine in sets or “holes” of five, comprising (a) the gatherer, (b) the blower, (c) the “finisher,” (d) the “wetter-off,” and (e) the “taker-in.” Generally speaking, the

first three workers mentioned are men and the last two are boys. A boy starts as "taker-in," and, as he progresses in ability, is transferred from one stage to the next, but rarely does he reach the "finishing" or "making" stage before he attains his majority. The "finisher" is usually termed the "bottle-maker," and is in charge of the "hole," whilst each of the other members has his own special part to play in the making of the bottle.

(303) **The "Working Hole."**—The five workers operate around what is known as the "working hole," out of which the glass is taken from the furnace, usually of the tank variety. This hole in the tank side or end wall is immediately above the surface of the molten glass, is almost semi-circular or of a horseshoe shape, and about ten inches by eight in width at the base or "pat." Where extra large glass containers, such as gallon jars, are made, the hole is somewhat enlarged. Close to, and parallel with, the working holes of the furnace is built a high wall or "shadow," and as there is an air space between this wall and the furnace the men derive a certain measure of protection from the heat radiated from the furnace and from fumes or smoke which may be emitted from the working hole. An opening, about two feet wide, in this wall or "shadow," in front of the working hole, gives the men access to the metal.

Bridging this opening, almost level with the bottom of the working hole in the furnace, is an iron plate about nine inches wide and one inch thick, called the "resting plate." Various arrangements are attached to this plate for holding tools, the "pipes" or "blowing-irons," the "ring iron," and the "punky" which carries the bottle immediately prior to the finishing of the neck.

Inside the furnace, and immediately in front of the working hole, is either a ring or small pot, according to the construction of the furnace. If the tank has a bridge it is usual to use rings out of which to gather the metal. These are made of fire-clay, and have an inside diameter of twelve or fourteen inches, being about three inches broad and four or five inches in depth. They float on the surface of the metal, being about two-thirds submerged, and so prevent the gathering of surface-scum, which is of course drawn towards the place where the molten glass is being removed.

Pots, or "potettes," are mostly used in tanks which have no bridge. They penetrate much deeper into the glass than rings, and are slightly conical in shape with a hole in the bottom, which enables the more refined glass to rise in the pot as gathering proceeds. They serve to eliminate scum, and also to reduce the temperature of the enclosed glass as compared with that in the open tank.

(304) **The Operation of "Gathering."**—The "gatherer," whose duty it is to collect the desired amount of glass on the blow-pipe, commences the making of the bottle. This blow-pipe is a strong iron tube which varies in size with the nature of the ware to be made. As a rule it is about five feet in length, three-quarters to one inch in external diameter, with a bore about a quarter of an inch. The end or "nose" of the pipe, upon which the glass is gathered, is usually thicker—*i.e.*, of larger diameter, than the rest of the pipe, its size being adjusted to suit the type of ware made. For small articles the nose must

not be too wide, or too much glass will be gathered and difficulty experienced in blowing the article. Larger ware requires a thicker and heavier nose, owing to the greater quantity of glass to be gathered. The larger the quantity of glass gathered, the slower it cools and the hotter the pipe nose tends to become. A pipe with a thin nose would accordingly become too hot, resulting in dark, dirty "iron-streaks" in the article blown.

Before introducing the pipe into the glass the gatherer must see that it is heated somewhat, for if the pipe is too cold the glass does not adhere to it properly, and where it does hold, the glass next the iron is chilled and becomes too viscous for blowing. On the other hand, the pipe must not be too hot or the "iron-streaks" referred to above will be encountered. Accordingly, a number of pipes are placed upon the "resting plate" with their noses just inside the working hole of the furnace. Each time the gatherer approaches the hole he places a cold pipe upon the resting plate at one end of the row and gathers upon the hottest pipe from the opposite end. The number of pipes heating in the hole is such that the hottest is at the correct temperature for gathering as it is taken up, and regular working is thus obtained.

There are two distinct methods of gathering glass upon the pipe. The first, known as "dipping," consists of gently plunging the pipe into the metal a few inches and then quickly rotating it as it is withdrawn, in order to retain upon the pipe the correct quantity of glass. This method entails blowing down the pipe before its removal from the furnace or immediately afterwards, in any case before the gathering is run to its correct shape. "Blisters" or bubbles may be produced in the gathering by this blowing, and in the glass in the tank by the action of dipping. Any "blisters" in the glass in the tank may then be found in the subsequent gathering.

The second method, by "turning" or "twisting," is the one usually followed. The pipe nose is only allowed to touch the surface of the glass within the ring or pot, and then, whilst the pipe is rotated, it is gradually raised and withdrawn from the furnace. As glass gathers upon the pipe by the rotation, the nose is gently raised, the correct amount of glass is so obtained, and in a more compact, bulbous form than is possible by the former process. It is not necessary to blow down the pipe, when this method is used, before the gathering is brought from the furnace.

After the glass has been gathered upon the pipe it is taken over a tub of water, where, by suitably sloping and rotating it in one direction only, the glass is caused to run to the proper shape, which is somewhat akin to that of a pear. If this is not correctly done the blower later finds some difficulty in working the glass on the marver.

The pipe, with the pear-shaped gathering correctly formed, is then rested upon a T-piece, and is moved gently to and fro by either the gatherer or the "wetter-off" until the glass is ready for the next process. This "to and fro" motion, if incorrectly applied, tends to produce a hollow in the end of the gathering when the blower, in the next operation, "crannies-off" the glass on the edge of the marver.

During this shaping operation the gatherer can, if he desires, cool the upper portion of the pipe by ladling water on to it with his free hand. He must also examine the gathering for the presence of furnace drops, blisters, stones, etc. Should any such imperfections occur he removes the small portion of glass immediately surrounding them by means of iron pincers.

(305) **The "Blowing" Operation.**—The "blower" takes the pipe from the gatherer (or "wetter-off") and proceeds to roll the glass upon the "marver." This "marver" is a large, flat stone about three feet long by one foot broad, and about six inches in thickness. The upper surface is specially prepared, smoothed, and is tilted away from the blower.

By drawing the gathering of glass along the edge (known as the "cranny") of the marver, the pipe being rotated all the time, the glass is driven to the extreme end of the nose of the pipe. Rolling to and fro upon the smooth surface of the marver now renders the gathering smooth, regular in shape and solid.

If the motion on the T-piece has been incorrectly done, the hollow in the end of the gathering will have appeared. In order to remove this, rolling upon the marver may take so long as to render the glass too stiff for the proper blowing of the body of the bottle, although the bottom of the bottle may be correctly formed. The blower may, on the other hand, "point" the gathering (see next paragraph) earlier than usual in order to obtain a correct blowing of the body of the bottle, but in this case the bottle bottom may be incorrectly shaped ("wedge"-bottomed). Generally speaking, however, the blower can, by varying the motion on the marver or the pressure brought to bear upon the gathering, correct the defect referred to above.

At the close of the marvering process the end of the gathering is shaped to a point, and at the same time the blower applies his lips to the end of the pipe and, by blowing, distends the gathering into a hollow bulb or globe which is known as a "parison." Much of the bottle-blower's art lies in the making of the parison, since different kinds of bottles require different thicknesses of glass in corresponding parts.

In some cases the parison is again gently rolled upon the marver, and should the bottle to be blown require a narrow neck, the part of the parison which will eventually form the neck of the bottle is rolled along the cranny until it is the desired diameter. At the end of the marver is a smooth, flat stone or an iron plate, and upon this the bottom of the parison is flattened almost to the size of the bottom of the bottle to be made, whilst the length of the parison is correctly adjusted by holding the pipe vertical and allowing the glass to lengthen by virtue of its own weight.

The parison at this stage approximates in size and shape to the finished bottle, and it is then blown to shape in the mould.

The mould, if of the "pull-to" variety, is made in halves. One of these is mounted on an iron plate, the "mould-plate," whilst the other is hinged horizontally to the first. A rod or chain attached to the hinged half of the mould allows the whole to be closed when the parison is brought into position in the fixed half.

In the "treadle" mould the portion enclosing the body of the bottle is made in one piece, a hollow cylinder, and is fixed. The upper, shoulder and neck, part of the mould is made in two parts, each hinged horizontally to the fixed body of the mould. The parison is lowered to the bottom of the mould and the upper portions closed by means of a treadle operated by the workman's foot.

(306) **The "Making" or Finishing Process.**—After blowing has been continued for a sufficient length of time to allow the bottle to become solid or "set," the blower hands over the pipe with the attached bottle to the "wetter-off," who removes the bottle from the mould. The pipe is carried to what is known as the "casher-box," which is a scoop-shaped piece of tin-plate about ten or twelve inches in diameter fixed upon a stand. The part of the bottle next adjacent to the pipe nose, is rested gently upon the back ("cutter") of the casher-box, and by means of a small, fine-spouted, watering-can or more usually a knife-shaped piece of flat iron, termed the "mullet," water is allowed to run upon that part of the neck against the pipe nose. The application of the water causes

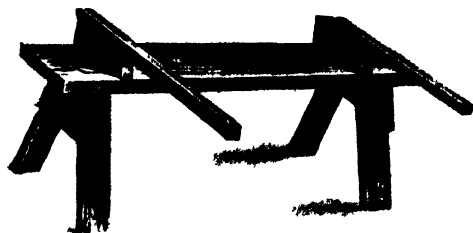


FIG. 172.—A BOTTLE-MAKER'S "CHAIR."
(By courtesy of the H. L. Dixon Co., Pittsburg, Pa.)

many small cracks or "crizzles" to appear on the neck of the bottle, and when the wetter-off strikes the pipe with the mullet the bottle falls away into the recess of the casher-box.

Where this "wetting-off" or "cracking-off" method cannot be used, as, for instance, with wide-mouthed bottles or jars, the following mode of procedure may be adopted. As soon as the bottle has been blown to the shape of the mould, and before the glass upon the pipe nose is set, the pipe is gently drawn upwards whilst the blowing pressure is sustained. This leaves the bottle attached to the pipe by a thin-walled tube of glass just sufficient to support the weight of the bottle without breaking. After removal from the mould the least touch serves to break the thin tube and to detach the bottle. This mode of separating bottle from pipe is known as the "paper-flange" method. Its chief drawback is the fact that pieces of the thin glass frequently fall into the bottle or jar, and may also adhere to the inside of the article if the latter is sufficiently hot.

The bottle, detached from the pipe, is taken by the bottle-maker from the casher-box by means of a tool known as a "punky" ("pontil"). This latter is made usually in the form of a split cylinder of iron fixed

upon the end of an iron rod, the diameter of the cylinder being such as to allow it to gently grip the bottle. The punty, with the bottle, is rested on a hook near the working hole of the furnace, the finisher gathers a little glass upon a small iron rod, known as the "ring-iron," and runs it evenly around the rim of the bottle neck. Sitting in the "chair" (see Fig. 172), which has horizontal, elongated arms, the bottle-maker then proceeds to finish the bottle neck. He rests the punty across the arms of the chair, and with his left hand rolls it to and fro. In his right hand he takes up a tool, fashioned like a pair of tongs, and provided with dies or plates which are fixed on spring arms about a central spike or plug which fits inside the bottle neck. The plug is introduced into the neck of the bottle, and by squeezing the tongs the dies are pressed against the thread or ring of soft glass on the bottle neck. As the punty is revolved on the chair arms the thread of glass is pressed and moulded into the desired shape of the "neck-ring" of the bottle.

The finished bottle is ejected from the punty on to a stand. It is then taken to the kiln or lehr on the end of a long iron rod or fork by the "taker-in."

(307) **The Speed of Working.**—The speed with which bottles are produced by the hand process naturally depends upon the size and shape of the article. For one-pint bottles, weighing about sixteen ounces each, the average rate of production is about one gross per hour. Since each of the five workers performs a definite portion of the process there is a series of five bottles in the making at any particular moment. Each "hole" uses thirty-six blowing irons. As the "wetter-off" cracks the bottle from the pipe he places the latter in an enclosure ("chest") of iron plates or netting, for the glass ("moils") remaining upon the pipe to crack away. He then removes a pipe, from which the glass has cracked, and replaces it in the working hole, thus maintaining constant the number of pipes at the gatherer's disposal.

(308) **The Blowing of Carboys.**—For carboy making the method just described is modified. Instead of five men per "hole" there are seven. Three of these are gatherers, known respectively as the "first-time," "second-time," and "proper" gatherer. The first-time gatherer does very little more than cover the end of the pipe with glass, although much depends upon his judgment of the temperature of the pipe upon which he gathers. He hands the pipe to the second-time gatherer, who gathers more glass and runs it round the nose of the pipe, meanwhile allowing it to cool. When cooled sufficiently the gatherer proper takes over the pipe and makes the final gathering. During the time the gathering is cooling to the temperature suitable for working, water is continuously ladled on to the upper part of the pipe in order to cool it.

The "parison-maker" then takes the pipe and fashions the parison in much the same manner as that already described. The parison, however, stands above the ground with its working surface horizontal, and whilst the parison-maker is pointing the parison another worker, behind him, blows down the pipe to form the hollow bulb. At this stage the glass has become very viscous. It is therefore reheated in the working hole.

The "blower," having first taken some water into his mouth, lifts

the parison from the hole when at the correct temperature, and, standing upon a raised platform, he allows water from his mouth to flow down the pipe and into the parison. The volatilisation of this water, together with the blower's "wind" pressure, enables him to blow out the parison to the desired holding capacity, which may vary from five or six to twenty gallons or even more. The first part of the blowing of the carboy is done whilst the parison rests upon a large iron plate, but finally the article is shaped by being blown into a basin-shaped mould. The neck and shoulder of the carboy are formed by the action of the blower in lowering or raising the pipe whilst the body of the article is in the mould. When the glass is set, the pipe, still carrying the carboy, is



FIG. 173 —GATHERING GLASS (FLINT HAND PROCESS).

(By courtesy of Messrs. Beatson, Clark and Co., Ltd., Rotherham.)

rested upon an iron T-piece and rotated whilst a ring of glass is cast around the neck. The neck is roughly finished by using an iron tool.

The carboy is carried to the kiln on the pipe, and is there cracked off from the pipe by the application of water between neck-ring and pipe nose.

(309) **The "Flint-Hand" Process.**—The "flint-hand" method of bottle-making usually obtains in works where the glass is melted in pots. If used with tank-melting, the glass is gathered from covered or "hooded" potettes, the mouths of which are built to an opening in the furnace wall. The glass enters the potettes through a hole in the bottom and is obtained at a lower temperature on gathering than that of the main bulk of glass in the tank.

The flint "hole" consists of two "gatherer-blowers," a "maker" or

"finisher," and a "taker-in." The two first-named workers each gather, blow, and "crack-off." Glass is gathered (see Fig. 173) on the pipe and shaped immediately upon an iron marver raised about three feet from the ground and tilted slightly away from the workman (see Fig. 174). The parison is then blown, and the portion which will form the bottle neck is narrowed on the edge of the marver prior to blowing in the mould (see Fig. 175). "Paper-flanges" are usually made, but where wide-mouthed ware is made another method is adopted. When blowing in the mould, the glass between bottle neck and pipe-nose is blown only a little thinner than the neck of the bottle. The pipe and the adhering bottle are taken to the "chair," and whilst the pipe is rotated



FIG. 174.—POINTING THE GATHERING ON THE MARVER.

(By courtesy of Messrs. Bealson, Clark and Co., Ltd., Rotherham.)

upon the arms, the blower, with a pair of dull-edged shears, makes a groove in the glass near the neck of the bottle. A slight knock on the pipe causes the bottle to break away at the sheared mark.

The bottle is picked up by the finisher in a punty and the neck is reheated in a glory-hole. When it reaches the desired temperature the neck is finished on the chair (see Fig. 176) in a manner similar to that in the ordinary bottle process.

(310) **The "American" Style.**—This method, of which there are many modifications, is akin to the flint-hand process just described, and is probably termed "American," since it results in increased production. The "hole" consists of six workers, usually three men and three boys, there being an increased proportion of unskilled labour used.

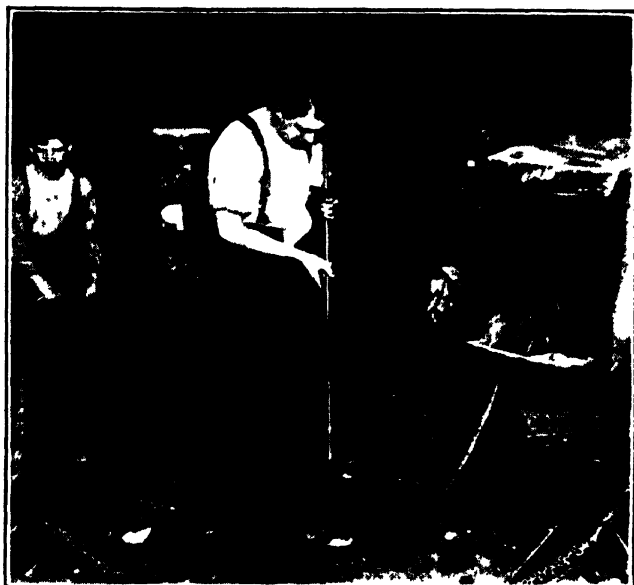


FIG. 175.—LOWERING THE PARISON INTO THE TREADLE MOULD.
(By courtesy of Messrs. Beatson, Clark and Co., Ltd., Rotherham.)



FIG. 176.—FINISHING THE BOTTLE NECK.
(courtesy of Messrs Beatson, Clark and Co., Ltd., Rotherham.)

Immediately the glass is gathered it is rotated in a hollow marvering block, the hollow receiving a constant supply of water. The gathering is therefore rapidly cooled and fashioned for the blowing of the parison.

After severing the bottle from the pipe (the former being left in the mould, usually of the treadle variety) by the paper-flange method, the bottle is removed from the mould by a boy and placed in a punty. Another boy carries it to the glory-hole, from which the finisher obtains it for completing the neck-ring. Two glory-holes are kept in operation, and therefore there is always a bottle reheating. Immediately the finisher completes a bottle, the boy who puts the bottles in the glory-holes takes over the punty and bottle and places them in a rack by the side of the mould. The "taker-in" removes the bottle from the punty, leaving the latter at hand for the boy who removes the bottles from the mould.

The leaving of the bottle in the mould obviates the use of the "cash-box," and thus enables the gatherer to proceed at once to the furnace for another gathering. By the employment of two extra boys, as compared with the ordinary flint-hand process, the rate of production is increased one hundred per cent.

In the flint-hand process only three pipes are in use instead of thirty-six in the common bottle process, whilst the services of the "wetter-off" are not required. The remelting of the neck, instead of casting a ring of molten glass upon it, results generally in a smoother and better appearance in the finished bottle. Whilst the flint-hand process is so far advantageous, it cannot be successful with the heavier types of bottles. Beer and mineral-water bottles, which are thick and heavy, and milk bottles with heavy, indented rings, are made by the common bottle process.

(311) **Hand-made Bottles in America.**—The following extract, taken from a paper by Turner,* further illustrates the advantages to be obtained by the use of unskilled labour and efficient organisation:

"Bottles are not all made by machinery in America, and one large works visited, as well as several smaller ones, was operated mainly by hand. This much is to be said, however, that the hand work is almost entirely confined to small ware of 6 ounces capacity and less.

"In the hand shops, the writer was surprised at the density of labour to be seen at the working end of the furnaces. The usual American 'shop' (corresponding to our 'chair') consisted of seven men, of whom three are skilled, two being blowers and one the maker or finisher; and at one works no fewer than twelve 'shops' were at work on one tank, by no means of large size. Such close packing of labour, with the blowers themselves working close up to the 'ring' or 'hole,' can only be accomplished by very efficiently cooling the workmen by streams of air and by severely restricting their movements. Specialisation applies to hand work as to machine, and each operator in the 'shop,' as may be judged, performs but a fraction of the work involved. Close up to the furnace are the two blowers, provided each with a short blowing iron. At their right hand, as they stand with backs to the furnace, is a boy, who receives from each blower in turn the iron just used, cleans it from the adhering glass moiil by one sweep of an iron forceps-like tool,

* *J. Soc. Glass Tech.*, 1919, 8, 166.

and places it ready for fresh use: Immediately in front of the blower, as they turn round from the furnace is the marvering slab and the mould, and sitting in front of the marver, presiding over the mould, is a boy or girl (coloured unskilled labour being largely used), who cuts the moil, opens the mould, and places the bottles on an adjacent table. A fifth worker (unskilled) takes each of these bottles in turn, fits it into the punty, and hands the latter to the finisher, who puts on the neck, a seventh unskilled worker removing the finished article for annealing. The two blowers describe, in their movements, a triangular path of very limited dimensions, and by long habit learn to keep out of each other's way. The output of bottles from such a set of workers may be very considerable; in the case of 4-ounce bottles, as many as 55 gross per 8-hour shift."

CHAPTER XXXII

THE MANIPULATION OF GLASS—*Continued*

II. Bottle-Making by Machine.

(312) **Inception.**—It occurred to Ashley, of Castleford, England, that much of the preliminary work in shaping parisons for mould-blown bottles might be mechanically performed. With this idea in mind he introduced the "parison" or initial shaping mould, equivalent in its action to the preliminary marvering and blowing of the glass. A further improvement by the same inventor was the use of compressed air for blowing up the bottle in the finishing or "blow" mould. These ideas have formed the basis of all subsequent bottle-blowing machines, which have thus divided the process into two distinct operations—namely, (1) shaping of the parison or blank, and (2) blowing up in the finishing mould. Two distinct types of bottle-forming machine have been designed. The earlier machines were of a somewhat complex form, which we shall name for convenience the "narrow-neck" type, although their use is not exclusively confined to the manufacture of narrow-neck bottles.

It was some years later that the simpler form of "wide-mouth" or "press-and-blow" machine was made commercially successful, and this type has still but a restricted use, owing to the fact that bottles with narrow necks cannot be made upon it.

(313) **Press-and-Blow Machines.**—In this type of machine the formation of the parison is accomplished by means of a cast-iron plunger. It was soon found that one parison mould could conveniently serve two blow moulds, and later designs contained one or more parison moulds and two blow moulds upon the same table. In the use of these simple machines human labour in the blowing of a bottle is reduced to the following: (1) Gathering the requisite quantity of glass and transferring this to the parison mould; (2) operating the plunger; (3) transferring the parison to the blow mould; (4) adjusting the blow head and releasing the pressure air; (5) removing the blow head; and (6) transporting the finished bottle from the blow mould to the lehr.

As an example of the press-and-blow machine we may consider a simple but efficient modern instrument made by Messrs. N. S. Kilner (Engineers), Ltd., of Leeds.

(314) **The Kilner Machine, No. 1.**—This machine, illustrated in Fig. 177, is suitable for wide-mouth bottles and jars. The parison mould is held in a slide on the left-hand side of the cast-iron table. This mould is of cast-iron, open at the top and with an internal recess appreciably less than that of the bottle to be blown, but so shaped that the

glass moulded in it, when later blown out, readily conforms to the shape of the blow mould. For shaping the neck of the jar a neck-ring mould is used, composed of two independent semicircular halves, hinged together

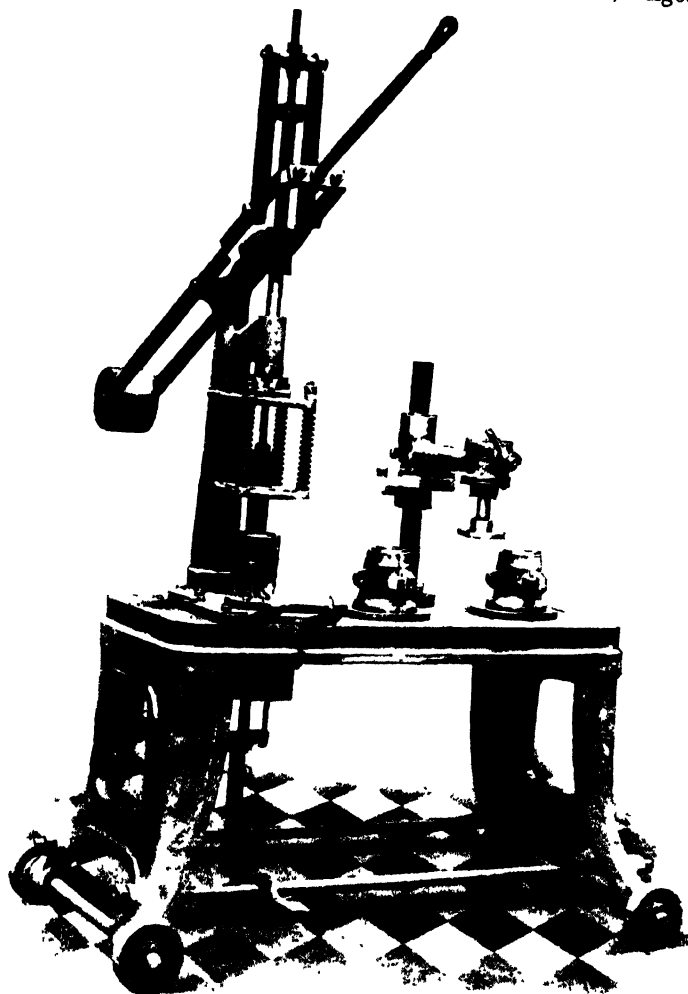


FIG. 177.—THE KILNER MACHINE, NO. 1.

(By courtesy of Messrs. N. S. Kilner and Co. (Engineers), Ltd., Leeds.)

and provided with a handle, and also with a catch for locking when closed. This ring mould is so shaped as to fit accurately to the top of both the parison and blow moulds, and serves to transfer the blank after pressing. Behind the parison mould is a column supporting a plunger which is

actuated by a hand-operated lever, and set symmetrically over the opening in the parison mould. On the plunger arm an adjustable plate is secured by four long bolts and powerful springs. In operation, this plate is brought on to the upper surface of the neck-ring mould, holding it in position, and, by its close fit against the plunger, preventing the squeezing out of glass from the mould as the plunger descends.

On the right-hand side of the table are two finishing or blow moulds somewhat similar in design to those used in hand-working. On a second pillar between and behind these moulds is a blow-head which can be swung over each mould in turn, when, by the operation of an air valve, a piston is caused to descend until a flat disc on the end of the connecting-rod fits accurately against the upper face of the neck-ring, as the latter lies on the mould. As soon as the disc seals the top of the mould, its action opens a secondary valve which allows compressed air to enter the mould for the blowing process. On closing the lever on the blowing head, the piston once more rises and the secondary valve is closed.

The machine can be operated by two youths and a boy, who work as follows:

Molten glass in sufficient quantity is gathered by the first youth on a gathering iron, dropped into the parison, and cut off with shears. The second youth places on this mould the ring-mould and pulls down the press-lever, so causing the plunger to enter the molten metal and force it to the shape of the mould and also up into the neck-ring. This ring-mould being cooler than the glass slightly chills it, and thereby allows the glass to retain its shape. The lever, travelling back to its top position, removes the plunger, and the ring-mould with the pressed blank is lifted from the mould and placed in one of the finishing moulds. The boy now swings over the blowing head, and by turning the lever causes the piston to descend. When in position the compressed air valve, as we have seen, is opened and the bottle is blown to shape. By again touching the lever the boy cuts off the supply of compressed air and raises the blow-head. The finished bottle is then removed from the mould and the ring-mould opened. Should a screw-neck bottle be desired a one-piece ring-mould is employed, suitably cut so as to give the required thread on the glass. When the bottle is blown, the ring-mould is screwed off before the bottle is removed from the blowing-mould.

(315) **Narrow-Mouth Bottle Machines.**—Press-and-blow machines, although suitable for wide-mouth ware, are of no value for the production of any kind of narrow-neck bottle. Only in a few cases, where the bottles possess a prominent shoulder, is it possible to force glass up into the narrow space between the ring-mould and the plunger. In the majority of cases the glass in the neck is so chilled that it refuses to take the desired shape. It is only by the use of a different system of forming the parison that the difficulty can be overcome. This consists in inverting the parison mould, the neck-ring mould and plunger being placed at the bottom. Glass is dropped in at the top as before, plugged, given a preliminary blow, and then transferred to the blow mould. Below is given a description of a modern machine of this type.

(316) **The Harlington Machine.**—This machine, sold by C. Melin and Co., London, is suitable for the production of narrow-neck ware.

It consists of a table, on the left-hand side of which is the parison mould (Fig. 178). Finishing moulds, two in number, are carried on a revolving platform supported by a central column. Below the table, near to the parison mould, is an air cylinder operated by a hand lever, which by one motion causes suction in the parison mould, but on reversal gives pressure air at the same point. When the glass is delivered, the plunger is in the "up" position, that is, projecting into the neck of the mould, but it is so connected that at the end of the forward motion of the lever

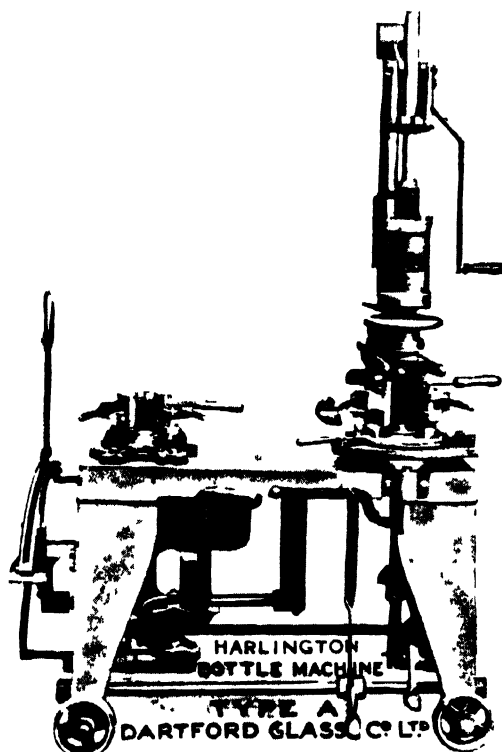


FIG. 178.—THE HARLINGTON MACHINE.

(By courtesy of Messrs. C. Melin and Co., London.)

it is automatically withdrawn. The machine operates as follows: A supply of glass is delivered into the parison mould, the requisite quantity being cut off with the shears. By gravity, the molten metal runs downwards into the space between the neck-ring and the plunger. It is assisted in this motion by suction, produced by pulling forward the lever. At the end of its stroke the lever releases the vacuum and withdraws the plunger, when a reverse movement of the lever admits air under pressure into the opening left by the plunger and blows up the parison to the shape of the mould.

The catch holding together the hinged halves of the mould is unfastened, the mould opened, and the parison lifted by means of the ring-

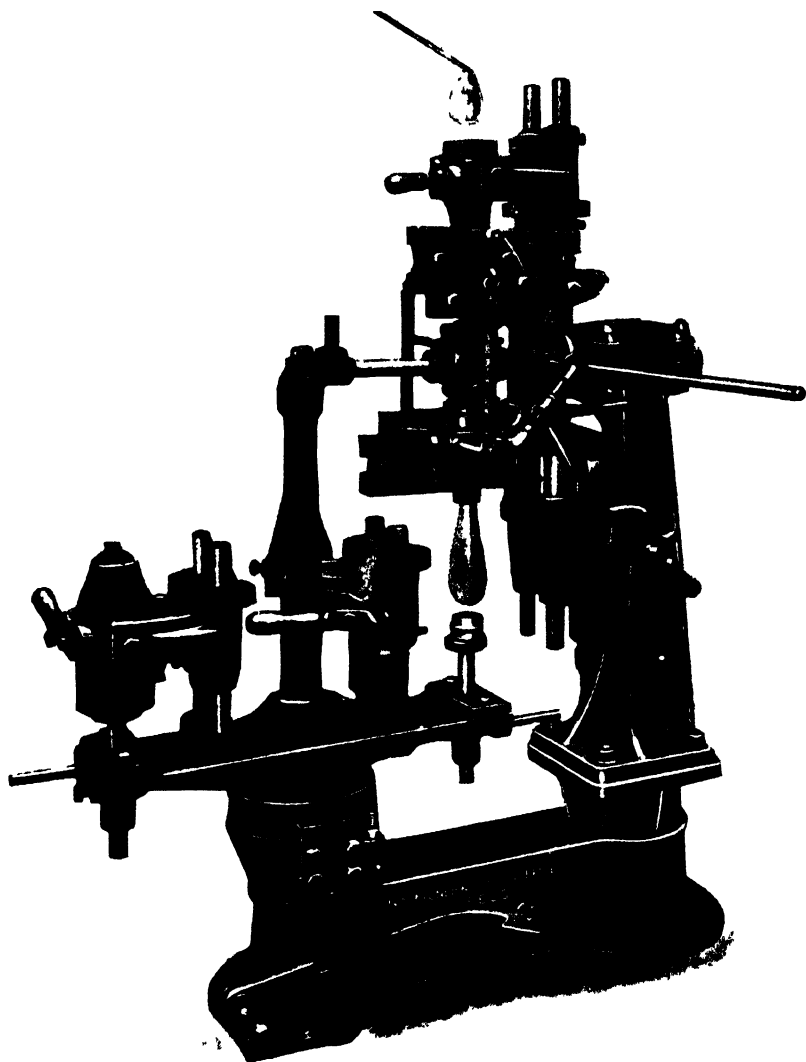


FIG. 179.—THE KILNER MACHINE (TURN-OVER TYPE).

(By courtesy of Messrs. N. S. Kilner and Co., (Engineers) Ltd., Leeds.)

mould and placed in an open blow mould, which is closed and locked. A boy now blows the bottle as before. When the blow-head is raised the

second finishing mould is rotated into position, the first opened, and the bottle removed.

(317) **The Kilner Bottle-Making Machine, Turn-over Type.**—Illustrated in Fig. 179 is a machine specially designed for the output of heavier bottles and jars, either wide- or narrow-mouthed, such as are used for ale, wine, jam, pickles, etc. This machine comprises two parison moulds and neck-ring moulds placed mouth to mouth at opposite sides of a horizontal spindle, about which they can rotate. Glass is placed into the upper, inverted mould and flows down into the neck-ring under the action of gravity. The parison is rotated through 180° , and the second mould brought uppermost ready to receive a gathering of metal. Whilst the second mould is being filled the first is opened and one of two blow moulds on a horizontal turntable brought in position, closed around the parison, and locked. Compressed air is now admitted and the bottle blown. On cutting off the air, the ring-mould is opened and the mould containing the bottle swung out of position, when it is opened and the bottle removed. As the bottle is removed the neck-ring mould and parison mould are closed and reversed to receive a further charge, whilst the second parison and finishing moulds in turn come into position for completing the succeeding bottle.

(318) **Multiple-Mould Machines.**—Desire for an increased rate of production led several American manufacturers to design machines with a number of parison and blowing moulds. Two turntables were generally used, one mounting the parison moulds, the second the blow moulds, and these were rotated mechanically. As each mould approached the gatherer it received its quota of glass, after which the blank was formed. Further rotation brought it into juxtaposition with one of the blow moulds, when the ring-mould was seized by a boy and the parison rapidly transferred from one mould to the other. Rotation of the blow mould table then brought the parison under a blow-head timed to descend at the correct moment and blow the bottle. On passing further stages in its journey the mould was opened and the bottle removed. Three people, one to gather, one to transfer, and one to remove, could thus keep a number of moulds in active operation without undue effort.

(319) **The W. J. Miller Machine, Model V-2.**—A modernised form of the foregoing type of machine, made by W. J. Miller, of Swissvale, Pa., U.S.A., is depicted in Fig. 180, and is stated to be suitable for making narrow-mouth ware of a capacity of 6 to 32 ounces. In this machine are five each of parison and finishing moulds, the former being inverted. When closed, the mould halves are held together by solid yokes fitting over lugs on the outside periphery of the mould halves. Parison moulds are mounted on the left-hand table, the mould position on the extreme left being the point of delivery of glass, and over this position is a pair of automatically operated shears. As the gatherer drops the glass into the mould he touches a small trigger with his gathering iron and this sets in operation the mechanism. In the first position, below the table is a plunger, cooled by compressed air jets, and this dwells in the neck for a sufficient length of time to produce a cavity and is then withdrawn. The two tables rotate through one-fifth of a revolution, that is, to the

next mould position, and pause whilst the succeeding mould is filled with glass. The previously filled parison mould is now immediately below a seal which descends and closes the upper opening of the mould, and as this is done, air is admitted from below and the parison is blown to shape. A further rotation of the mould tables now brings the parison near to the blow mould table, at which point the parison mould is automatically opened. A boy seizes the neck-ring mould, lifts out the parison, inverts it, and places it in the contiguous blow mould, which he closes with a treadle. The succeeding movement brings the blank

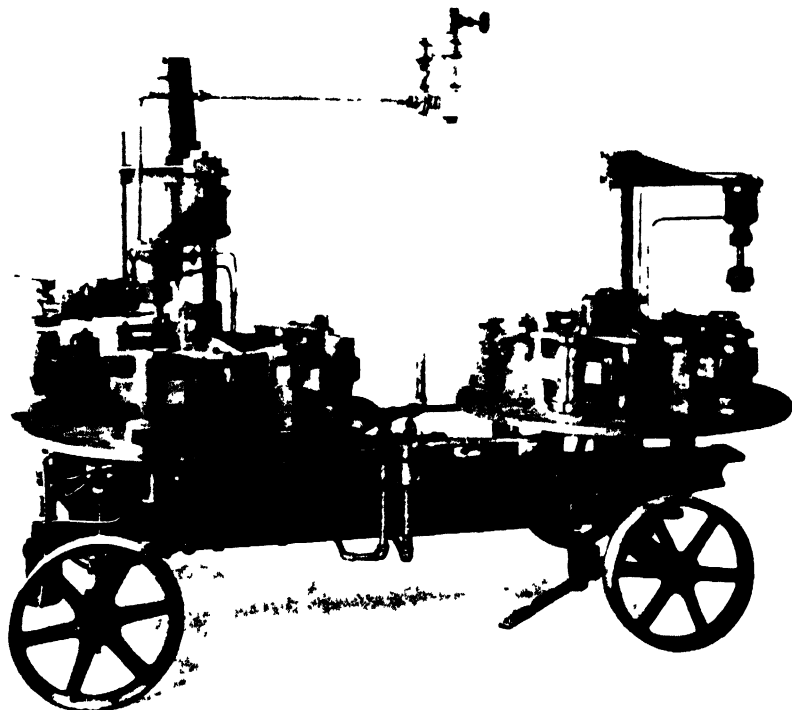


FIG. 180.—THE W. J. MILLER MACHINE—MODEL V-2.

(By courtesy of W. J. Miller, Swissvale, Pa., per S. H. Rylett, London.)

under a blow-head, which descends and blows up the bottle to shape. Finally, the blow mould automatically opens and the bottle is removed. Meanwhile the emptied parison mould rotates once more to the filling position, and is mechanically closed before this point is reached. To operate the blow-head an air pressure of 30 pounds per square inch is required, the air being led to the machine through flexible piping. Several additional devices are fitted to ensure smoothness of working, such, for instance, as safety appliances on the mould locks to relieve strain should foreign matter be caught in the mould joint during closing, an air filter to provide clean air, etc. This machine is claimed to be capable of an output of up to fifteen bottles per minute.

(320) **Machines with Automatic Transfer and Take-Out Devices.**—A further improvement in bottle machines of the multiple mould type was the provision of a device for the transfer of the blank to the blow mould, and also of an apparatus for removing the finished bottle from

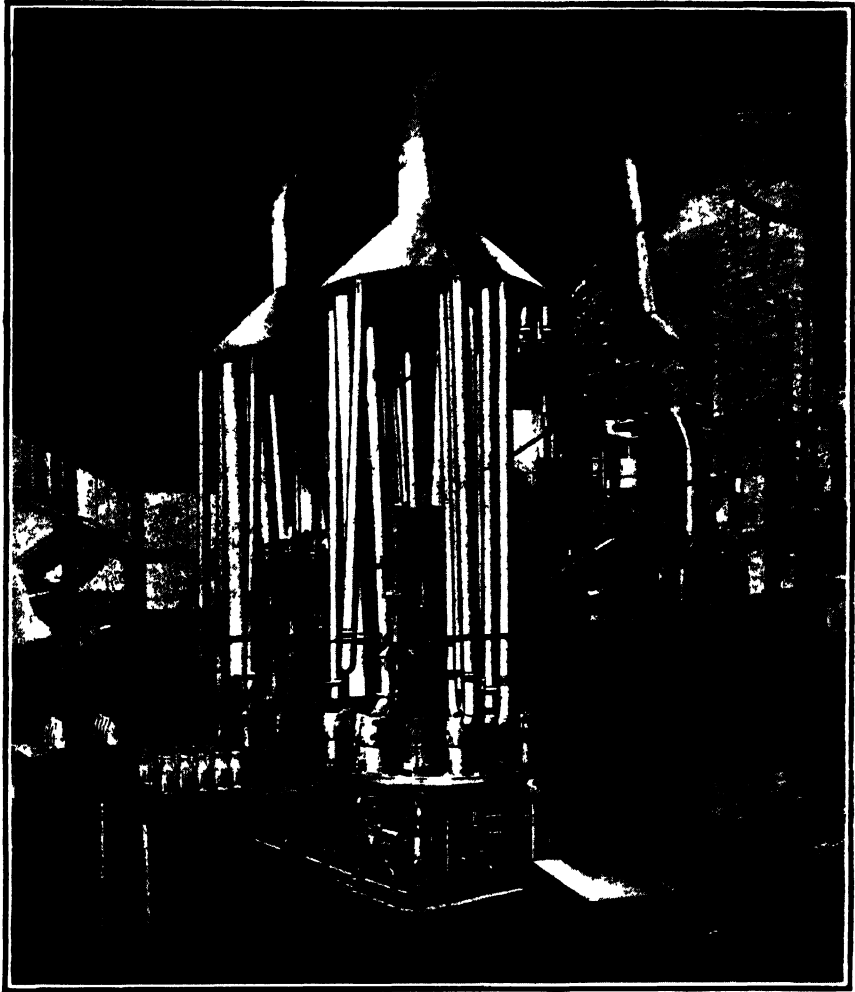


FIG. 181.—THE HARTFORD-FAIRMONT MILK-BOTTLE MACHINE

(By courtesy of the British Hartford-Fairmont Syndicate, Ltd, London, per E. Meigh, Esq., M.B.E., M.Sc.)

the blow mould. A number of these machines are now in use, as, for instance, the Cox, Graham, Hartford-Fairmont, E. Miller, W. J. Miller, Lynch, and O'Neill machines. As an example of a machine for wide-mouth ware only we shall consider the Hartford-Fairmont, in which

the parison moulds are placed neck uppermost and do not invert. Other machines, such, for instance, as the Lynch and O'Neill, are designed for either narrow- or wide-mouth ware, and in these cases glass is fed into an inverted parison mould. Since, however, it would be difficult to transfer an inverted blank to a non-inverted blow mould, these machines are so constructed as to re-invert the parison mould between filling and delivering to the blow mould.

(321) **The Hartford-Fairmont Milk-Bottle Machine.**—This machine (Fig. 181) possesses but one table, and on this are mounted eight parison and eight blow moulds, arranged alternately, the blow moulds being set a little back on the table towards the central bearing column. The parison moulds are of one piece, only the blow moulds being hinged to open. In each revolution of the table there are, of course, eight stop-pages to allow of each parison mould being filled in turn. Since the parison mould does not open, it is evident that the blank itself must taper downwards from the neck-ring, that is, it must be somewhat conical in shape. Projecting through the bottom of each of the parison moulds is a stud, the lower end of which passes through the table. At the correct moment, after the parison has been pressed, the lower end of this stud comes in contact with a sloping track, and the parison is thus gently pushed upwards until the neck completely projects from the mould. At this point a special "take-out" (Fig. 182), descends, seizes the parison, and raises it clear of the table. The "take-out" then rotates horizontally through half a revolution until the parison is directly over the adjacent blow mould, when it descends, deposits the parison in the mould, releases it, and again ascends. Blowing is now performed by a blow-head in the usual manner.

Taking the history of an individual charge of glass fed into the machine, the process is as follows:

Position 1: The charge is fed into the parison mould.

Position 2: A plunger descends and presses the parison to shape.

Position 3: The parison is cooled.

Position 4: Transfer of the parison to the blow mould is effected.

Positions 5 and 6: Cooling takes place.

Position 7: The bottle is blown.

Positions 8, 9, 10: Cooling again takes place.

Position 11: The blow mould opens and the bottle is removed by a boy. The mould then closes once more and passes to the next position.

(322) **The O'Neill Machine, No. 25.**—This machine comprises two circular tables, each carrying six moulds and each rotating round a central column (Fig. 183). As with the Miller machine, the tables rotate and pause at the same instant, but in this case, of course, turn each time through an angle of 60°. The machine is air-driven and controlled in all its actions. All individual operations are timed by air-valves, which supply air at the correct moment to cylinders controlling these movements, this control constituting a distinct feature of the machine. Glass gathered on a clay-nosed gathering iron is dropped into the mould through a pouring ring. When sufficient glass has been run in a trigger is touched with the iron and this sets in operation the shears which cut off the glass. The parison mould is in an inverted position, and as the

shears open a head is forced down upon the pouring ring, a valve is opened, and pressure air blows the glass down around the plunger situated below in the neck of the mould. The head now rises and the plunger

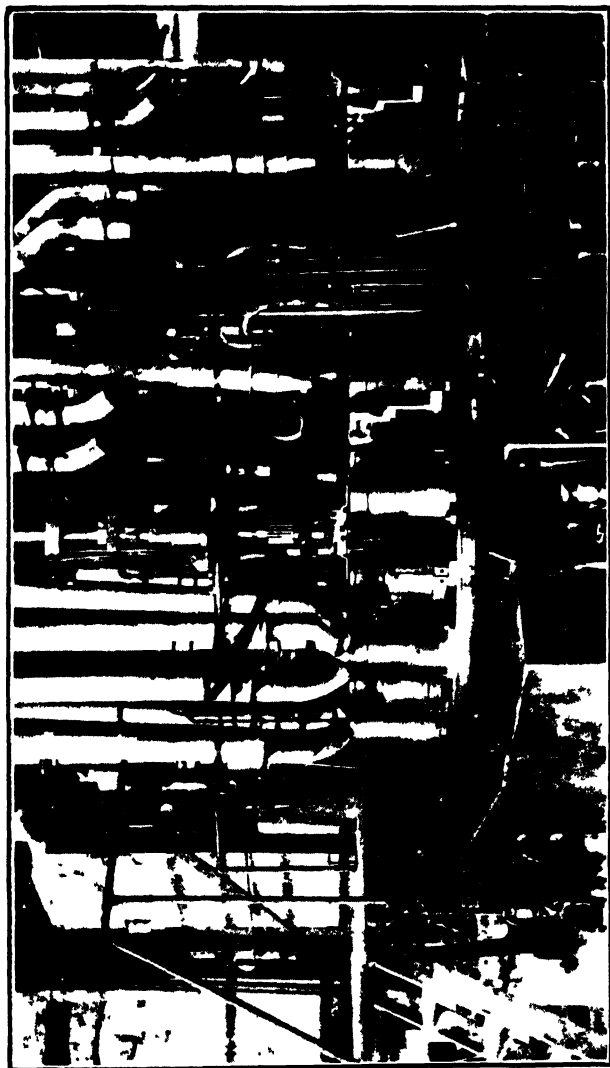


FIG. 182.—THE HARTFORD-FAIRMONT "TAKE-OUT."
(By courtesy of the British Hartford-Fairmont Syndicate, Ltd., London, per
E. Meigh, Esq., M.B.E., M.Sc.)

is pulled out of the neck, when the mould advances to the second position. At this point a solid head is pressed down upon the mould to close the opening, and air is admitted from below, thus blowing the glass to the shape of the mould. The head rises and the mould advances

to position three, rotating as it moves, until the charge has been inverted. In this position the mould opens, leaving the blank suspended by the ring-mould, which moves across until it is in position over the corresponding blow mould. This blow mould now closes over the glass, and,

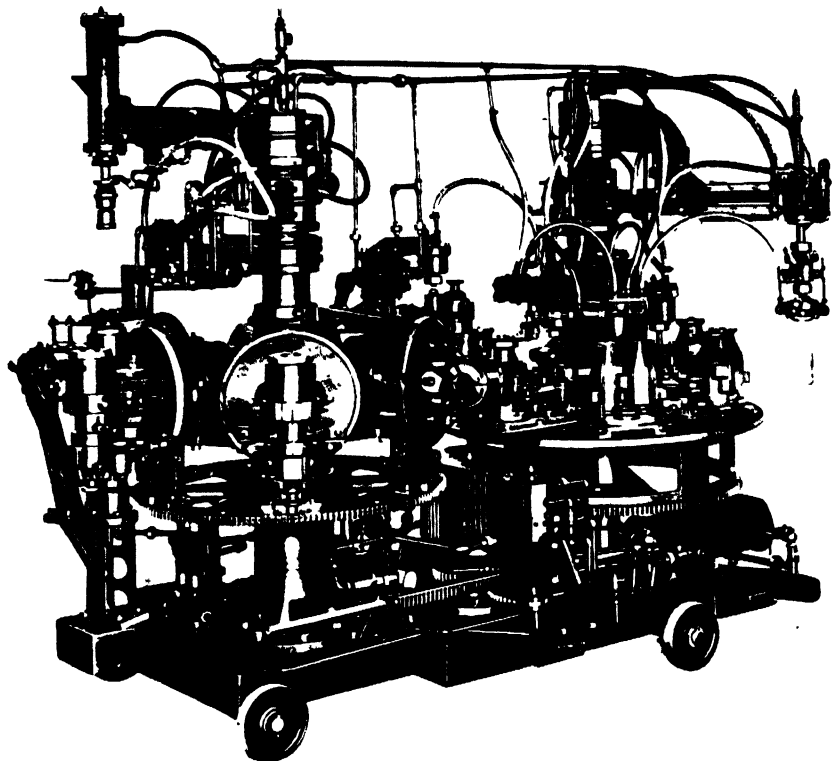


FIG. 183.—THE O'NEILL MACHINE, No. 25.

(By courtesy of the Ingersoll-Rand Co., Ltd., London.)

as it does so, the ring-mould opens and frees the glass entirely from contact with the first table. In the next position of the blow mould a piston descends, compressed air is released, and the bottle is blown. At the next-but-one stopping-point the finishing mould opens and a pair of automatic pincers seize the bottle at the same instant, carry it from the table, and place it on a suitable conveyer (Fig. 184), whence it is transferred to the lehr. This machine works with air at a pressure of 40 pounds per square inch, with 7 pounds for blowing, and, in operation,

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one gatherer suffices to work it. Its output is given as 30 to 40 gross of 16-ounce ware or 40 to 50 gross of 8-ounce ware per 9 hours.

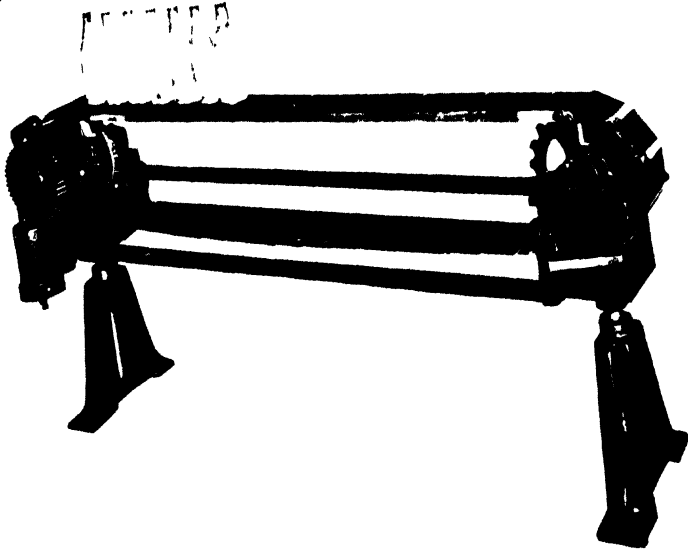


FIG. 184.—THE O'NEILL CONVEYER.
(By courtesy of the Ingersoll-Rand Co., Ltd., London.)

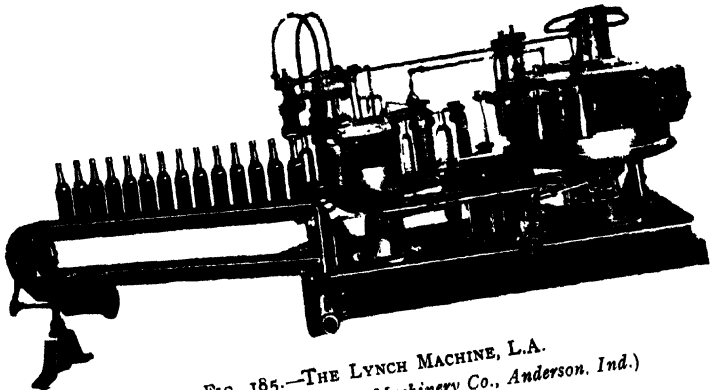


FIG. 185.—THE LYNCH MACHINE, L.A.
(By courtesy of the Lynch Glass Machinery Co., Anderson, Ind.)

(323) **The Lynch Machine, L.A.**—A machine in which the transfer is on a different principle is the Lynch machine, L.A., illustrated in Fig. 185, and diagrammatically in plan in Fig. 186. The parison and

blow moulds, six of each, are mounted on separate tables. Both sets of moulds are hinged, and open and close mechanically. It is to be noted that all the moulds project over the edges of the tables, and the path of the central vertical axes of the parison and blow moulds, when these are closed, coincide at the point of transfer. The neck-ring mould is itself hinged and opens independently of the rest of the parison mould, serving to sustain the blank between the time it is left by the parison mould and enclosed by the blow mould. The base plate of the blow mould is rigidly fixed and independent of the rest of the mould, which, however, on closing, fits tightly against it. In a somewhat similar manner to the O'Neill machine, the parison moulds are attached to a drum and rotation is obtained by the provision of a gear wheel and rack.

At the first or filling station of the parison mould glass is fed into the machine, which is then set in motion by tripping a catch. An air-cooled piston rises in the neck of the mould, shears cut off the glass above, and a blow-head descends and, by means of pressure air, forces the metal down into the neck of the mould. The table moves to the second position and here air is admitted from below and blows up the blank. In moving from the second to the third station the parison mould is inverted, and it then opens, leaving the blank suspended by the ring mould. At this point the base plate of one of the blow moulds comes beneath the suspended glass and the two halves of the same mould close around it. The ring mould has simultaneously opened and the glass is entirely free from the first table and continues its journey around the second. At two succeeding stages on the blow mould table a blow-head descends and the bottle is blown. Finally, the mould opens and a pneumatically operated "take-out" lifts the bottle and places it on to a conveyer belt. At each stage on the two tables where blowing is performed the mould is clamped by pneumatically worked jaws. An air-pressure of 35 to 40 pounds per square inch suffices to work the machine (for blowing, 7 pounds), and it is stated to produce 10 to 23 bottles per minute, ranging in size from 4 ounce to 64 ounce contents.

(324) **Feeding Devices.**—With the successful introduction of rapid semi-automatic bottle-making machines came the need for automatic methods for delivering the molten glass to the machines. It is interesting to note that even as early as the year 1885 an attempt was made by Messrs. Rylands of Barnsley to design a feeding apparatus, though with only partially successful results. At this period the rate of production of the bottle-making machines employed did not warrant the use of a mechanical method of supplying the glass. Indeed, the added difficulties connected with the introduction of feeding devices more than counter-balanced any advantages in their favour. This point will be clearly seen when we analyse the essentials necessary for the successful application of a feeding device. They are as follows:

1. The source of supply of glass must be constant and steady, with a surface level almost invariable, and the glass must not devitrify under the conditions of working.
2. The feeding device must be simple and strong in design, easy of regulation, and capable of dealing with glass of a kind suitable for the forming machine.

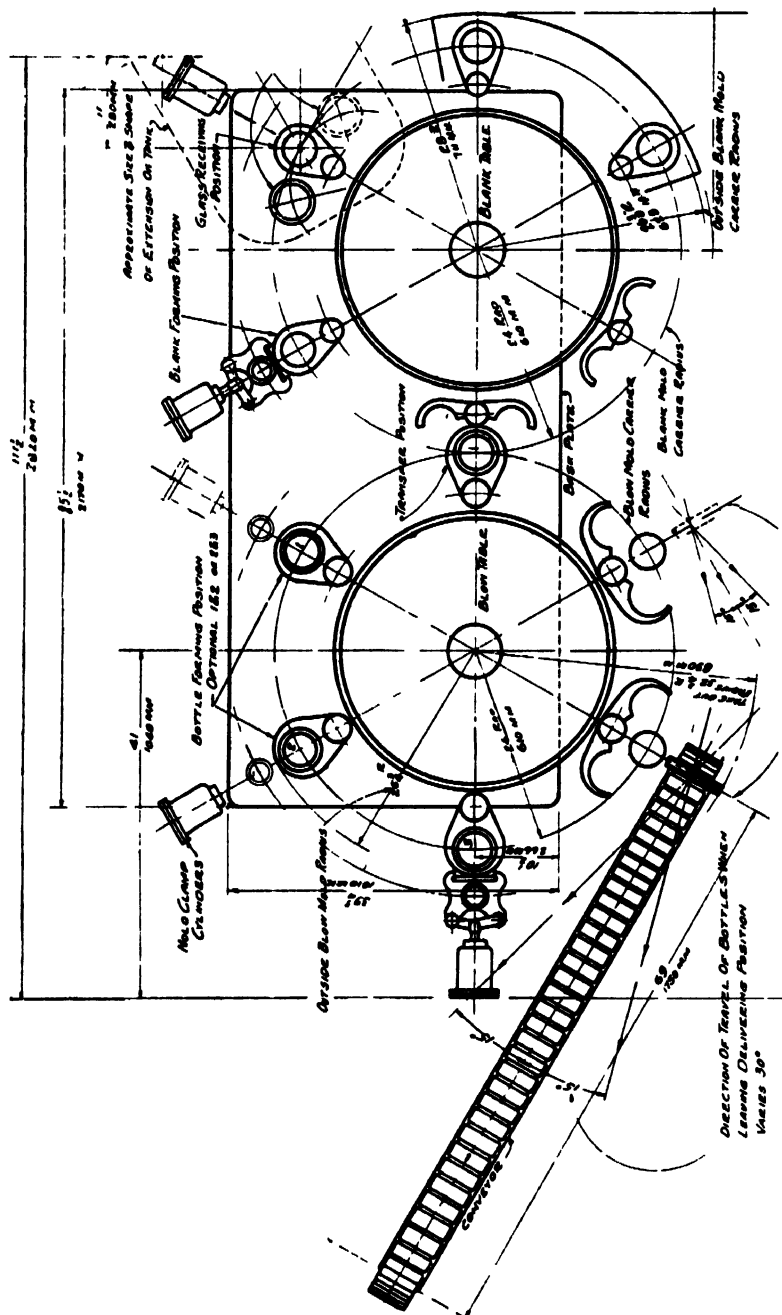


FIG. 186.—THE LYNCH MACHINE (PLAN).
(By courtesy of the Lynch Glass Machinery Co., Anderson, Ind.)

3. The device must further supply charges of glass of regular size, approximating in shape to the interior of the parison mould, and capable of variation with changes in the size and shape of the bottle to be produced.

4. Local chilling of the glass must be avoided as far as possible.

5. The bottle-forming machine or machines must be capable of taking the supply of glass at a regular, even rate.

The first condition is evidently one of furnace design and regulation, and calls for a thoroughness of treatment of a kind seldom attempted where hand-working is in use.

Conditions 2, 3, and 4 illustrate difficulties inherent in the actual feeding device itself. It is not surprising, therefore, that little more was attempted in this direction until a rate of working of bottle-forming machines such as to render hand-feeding difficult was attained. This rate of working was reached about the close of last century, and in 1901 the first successful feeding device was invented by Homer Brooke. Since then, and particularly during the past few years (from 1917), a number of devices, based on varying principles, have been patented. It is now possible to supply machines, not only for making bottles, but also electric light bulbs, pressed ware, etc., at a rate much greater than could be humanly accomplished, and, in the case of many of these feeders, with superior results as regards regularity of size and shape than would be obtained by hand, even at a much slower rate of working.

(325) **Classification of Feeding Devices.**—We may classify feeding devices as follows:

(1) **FLOW FEEDERS.**—This class represents the earliest type designed. It was rendered successful by the provision of a small projecting chamber or subsidiary tank, built at the working end of the supply furnace. In the bottom of this chamber was provided a hole. Glass from the main body of the tank flowing into the chamber ran in a stream from the hole into the parison moulds which passed below. One of the difficulties of this method lay in holding up the stream of glass, without undue chilling, during the period of substitution of a full mould by the following empty one. A further trouble was found in the coiling of the somewhat viscous stream as it fell into the mould, and this is particularly liable in the case of a long stream. The flow device was somewhat wasteful, it did not control accurately the shape and weight of the charge delivered, and it possessed several other minor faults. The original Homer Brooke feeder was one of this class.

(2) **MODIFIED FLOW FEEDERS.**—One great trouble with the simple flow device was that the charges delivered were not shaped very suitably for entering the parison mould of the forming machine. This resulted in a tendency to the formation of blisters or air-bells. The difficulties were particularly emphasised in the production of narrow-neck ware, and many modified forms of feeder, designed to give better and more uniform results, have been patented during the last few years. The most successful attempts seem to have been in the direction of the formation of a "gob." Instead of allowing the glass to run from the tank in a constant stream it exudes intermittently, each delivery being in the shape of a large drop or gob. Examples of this class are the devices

of Proeger (1914), Drey (1915) and Wadsworth, in which the glass gathers in cup-shaped shears placed just below the orifice. The shears open and shut again rapidly, allowing the gob to drop, and cutting off its tail as they close. More recent forms of apparatus, such as the Miller and Rankin feeders, employ a plunger in the glass itself immediately over the orifice. This plunger, moving vertically with a reciprocating motion, serves to form and deliver gobs of suitable size and shape. The Hartford-Fairmont feeder combines the action of a shaped plunger or needle with that of a paddle for driving constant amounts of glass through the orifice. These plunger feeders supply glass at a much lower temperature than do the simple flow feeders, the gobs being supplied at the working temperature, namely, 1100° to 1150° C.

(3) **GRAVITY-HEAD FEEDERS.**—Feeders in which the use is made of a head of liquid to force the glass through a passage and up into the mould have been designed by Wadsworth and others.

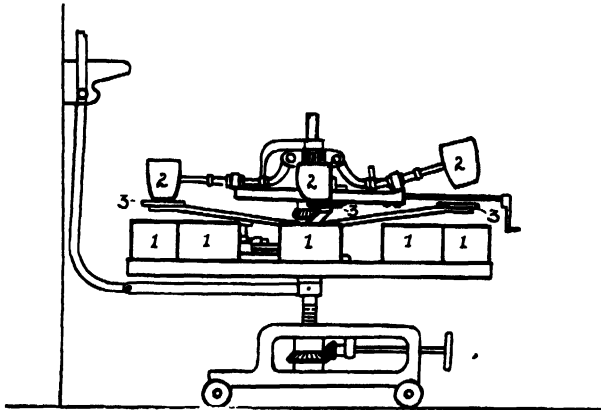


FIG. 187.—THE HOMER-BROOKE FEEDER.

(4) **PUNTY FEEDERS.**—These were designed to reproduce the actual work of the human gatherer. Apparatus of this type has been patented by Jensen and Henle, Haley, Peiler, and others.

(5) **SUCTION FEEDERS.**—The method of sucking glass from a tank into the parison mould has been most successfully developed in the Owens bottle machine and the Westlake bulb machine, and will be described along with these machines.

(326) **The Homer Brooke Feeder.**—In this feeder a continuous stream of molten glass issues from an orifice, below which is a table carrying moulds, 1 (Fig. 187), and rotating intermittently around a central vertical shaft. As each mould comes below the orifice it pauses until it is filled and then makes way for the succeeding mould. During replacement of the moulds the stream is severed by the combined action of a series of cup-shaped members, 2, and shear blades, 3, moving in opposite directions about the central shaft. As the cup and shear blade meet they sever the stream, after which the cup is raised to support the stream until the new mould is below. The cup then turns over and delivers the metal

it contains into the new mould, finally moving away. These actions are illustrated diagrammatically in the successive stages **A**, **B**, **C**, **D**, and **E** (Fig. 188).

Some more recent feeders have replaced the tilting cup by a divided cup, the two halves of which, when together, hold the stream of glass.

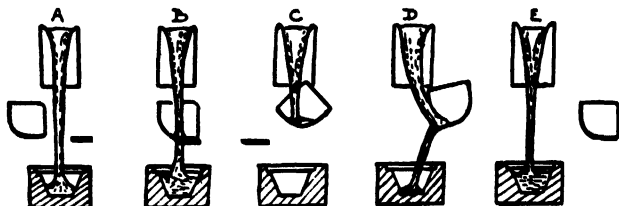


FIG. 188.—THE HOMER-BROOKE FEEDER.

When the cup opens the flow of glass again restarts and the mould is filled. A feeder designed by Wadsworth is of this type.

(327) **The Miller Feeder.**—As has been stated before, the Miller feeder assists the formation of gobs of glass by the use of a plunger. From the working end of the tank, 1 (Fig. 189), projects the feeder chamber 2,

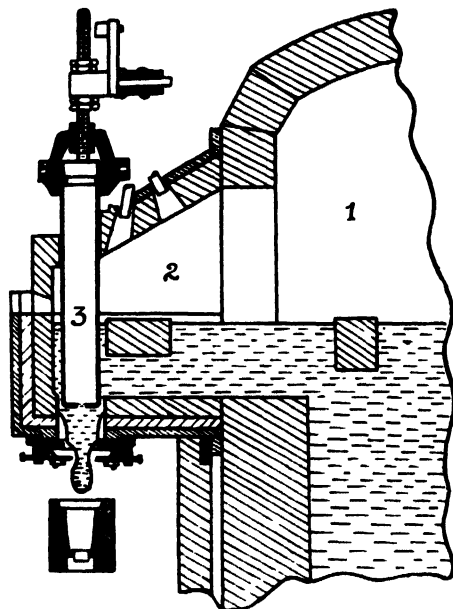


FIG. 189.—THE MILLER FEEDER.

into which the glass can freely flow, although surface impurities are kept back by obstruction blocks. At the end of the chamber remote from the tank is the orifice for extrusion of the glass, below which are arranged shear blades. A cylindrical plunger, 3, passes through the roof of the chamber and into the liquid directly above the orifice. The upper end

of this plunger is held by a mechanism which imparts to it a vertical reciprocating motion. The glass reaches the extrusion orifice at the regular working temperature, and thus has a tendency to gob formation rather than to flow out in a thin liquid stream. Whilst the mould below the opening is being replaced, the glass is held up by the withdrawal of the plunger coupled with a puff of air of definite volume and of progressively reducing pressure for a definite length of time. The air then stops and the glass falls in a thick stream. As the gob becomes heavier it pulls out and becomes thinner, and at this point the plunger rapidly descends, forces out more glass and prevents undue thinning. The plunger reaches the bottom of its stroke, then ascends, so shaping the neck of the gathering, and allowing it to be cut off easily with the shears. The neck created by the upward motion of the plunger is so pronounced that no distinct shear mark results and the shear blades do not become overheated. Immediately

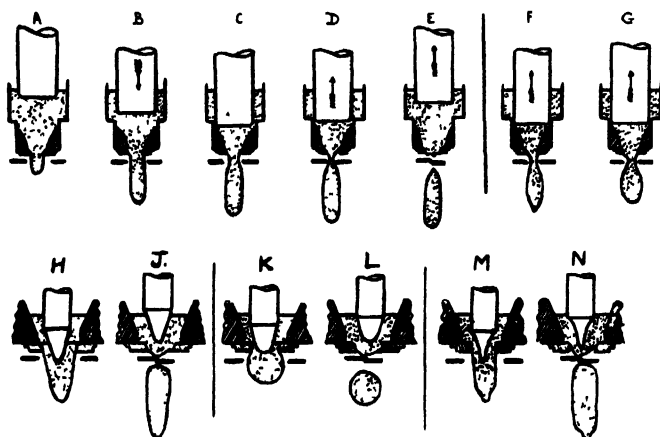


FIG. 190.—VARIOUS "GOB" SHAPES FROM FEEDING DEVICES.

the gob is severed, a fresh puff of air is set free and the glass is held in the orifice until a new mould arrives below. It is important that the air-blast should decrease in pressure, otherwise the amount of recession of the liquid could not be accurately gauged and gobs of uneven weight would be obtained.

It is possible in this feeder to regulate the size and shape of the gob to some extent to suit the shape of the mould for which it is intended. This is done by adjusting the relative times of motion of the shear and plunger, and the length of path of the plunger. In Fig. 190 are illustrated successive stages (A to E) of the formation of a gob, whilst F and G show formation of gobs of somewhat different shape.

(328) **The Hartford-Fairmont Feeder.**—This feeding device is somewhat complicated in design in that it forms the gob as a result of the combined action of a paddle and of a plunger or needle. The feeder chamber, 1 (Figs. 191 and 192), ends in a lip beyond which is situated

the extrusion orifice. Into the chamber dips a paddle, 2, which drives successive waves of glass of uniform size over the lip by a regular motion. The paddle is depressed into the liquid and moves towards the lip for a definite distance. It then stops and is drawn to the top of the glass, thence receding to its opening position for a second downward and forward stroke. Successive waves of glass so forced over the top fall through the orifice and are shaped by a motion of the needle, 3, somewhat similar in action to the plunger in the Miller feeder. The glass is at working

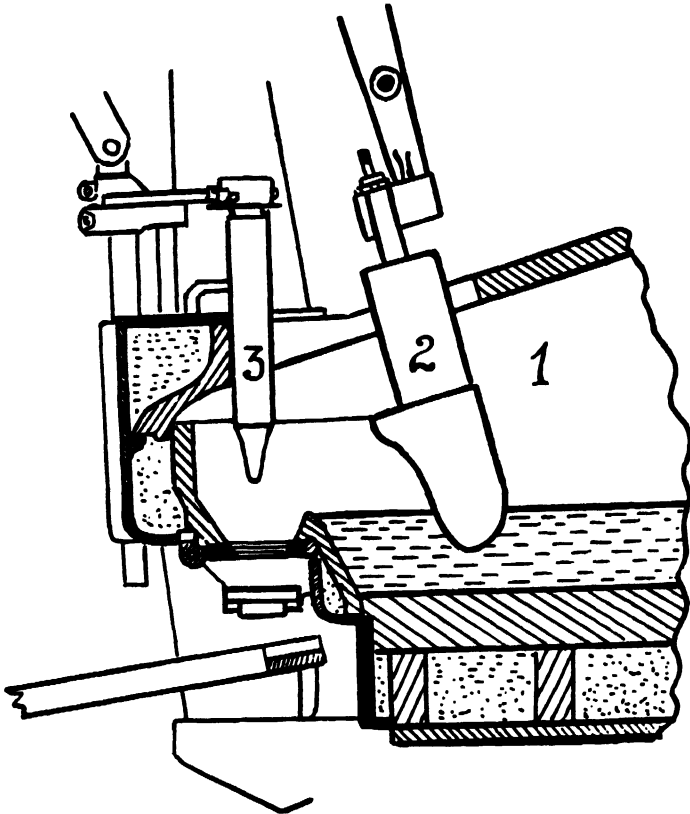


FIG. 191.—THE HARTFORD-FAIRMONT FEEDER.

temperature, and forms gobs of a size and shape determined by the following factors: (1) the length of paddle stroke and its depth of immersion, (2) shape of nose of needle, (3) relative timing of needle and shear movements. By the combination of these adjustments it has been found possible to obtain very accurate adjustment of the shape of the gobs obtained. For instance, it is possible to obtain gobs of each of the four following forms: (1) Spheroidal, for pressed tumblers, etc.; (2) cylindrical with blunt ends, for wide-mouth bottles; (3) a gathering with straight sides tapering at the lower end, for most press-and-blow products; and

(4) a cylindrical body with a distinct shoulder at the lower end, for narrow-neck bottles (see Fig. 190, **H** to **N**). The feeder may be used to supply a

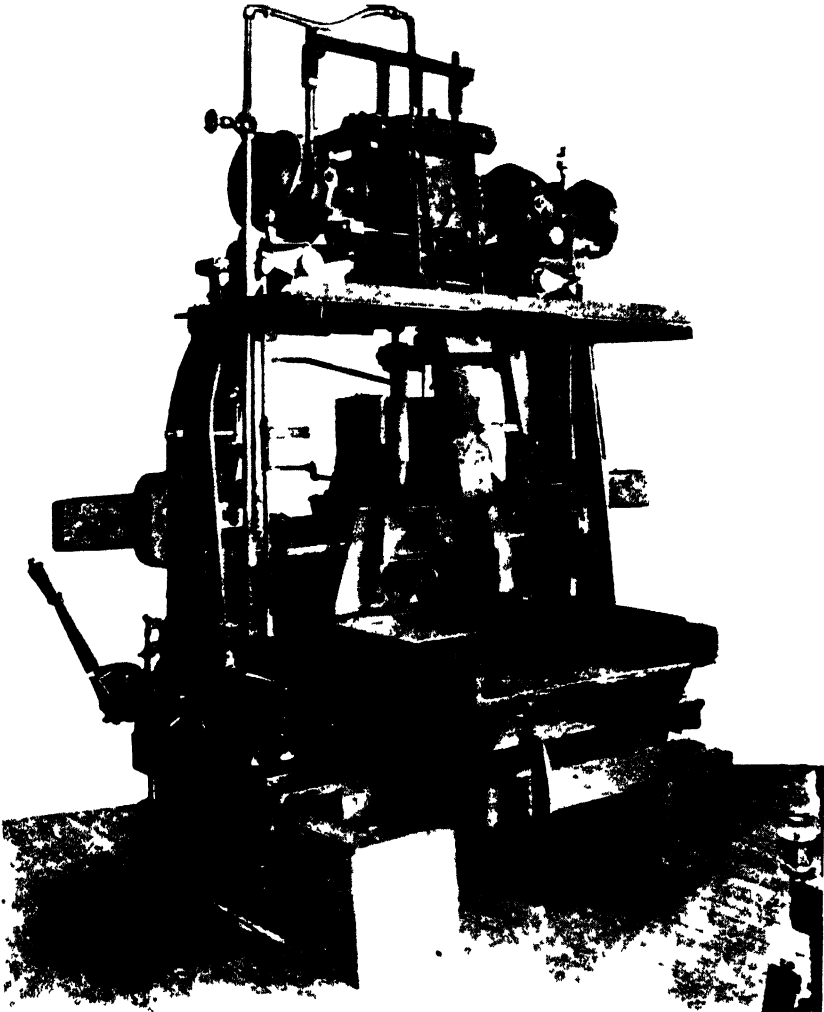


FIG. 192.—THE HARTFORD-FAIRMONT FEEDER (FURNACE SIDE, SHOWING PADDLE AND NEEDLE).

(By courtesy of the British Hartford-Fairmont Syndicate, Ltd., London, per E. Meigh, Esq., M.B.E., M.Sc.)

single forming machine, but for big production is usually made to serve three or four machines. This is done by using a hinged receiving trough

below the orifice, which trough moves in turn in register with water-sprayed, inclined, cast-iron troughs (see Fig. 193) leading to the machines.

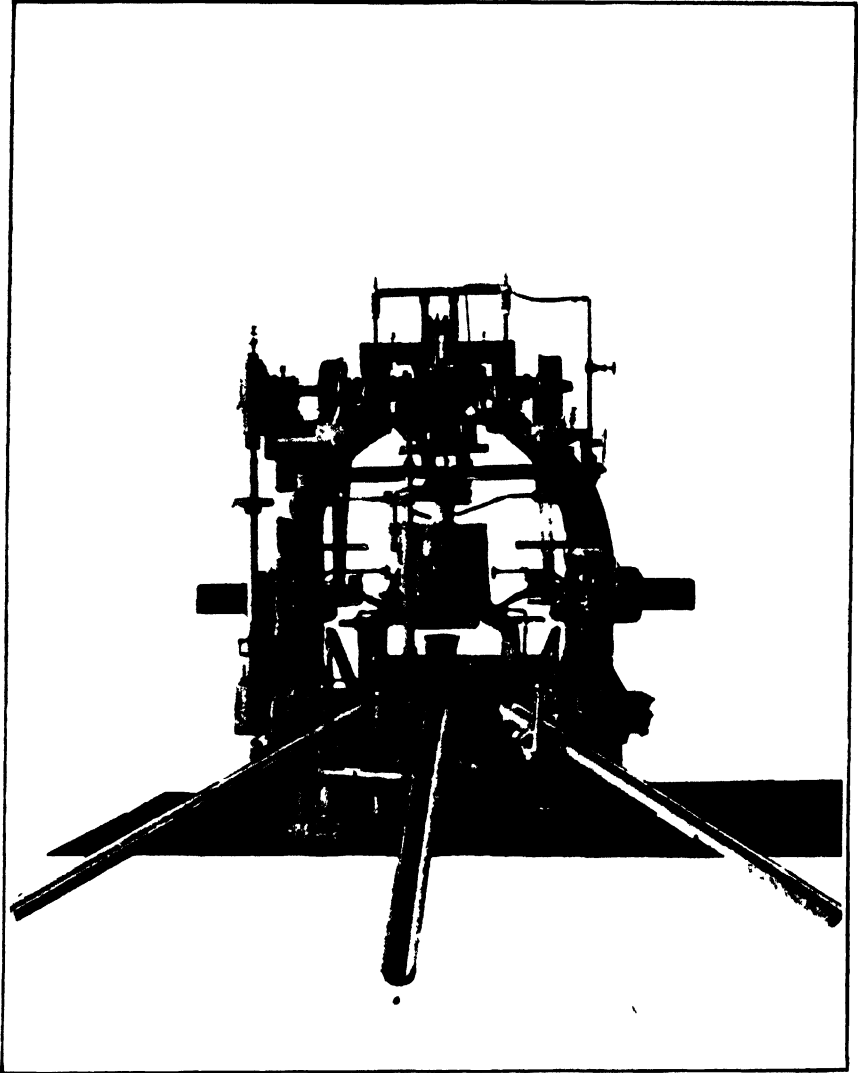


FIG. 193.—THE HARTFORD-FAIRMONT FEEDER (MACHINE SIDE, SHOWING TROUGHS).

(By courtesy of the British Hartford-Fairmont Syndicate Ltd., London, per E. Meigh, Esq., M.B.E., M.Sc.)

The hot gob creates a water-vapour cushion on which it rests as it slides down the trough—so tending to prevent deformation.

(329) **The Jensen and Henle Feeder.**—A good example of a punty feeder, designed to overcome the numerous difficulties besetting the mechanical punty gatherer, is the machine patented by J. O. Jensen and J. Henle (illustrated in Fig. 194). The motions of the gathering iron, **1**, of this machine are arranged to approximate as closely as possible

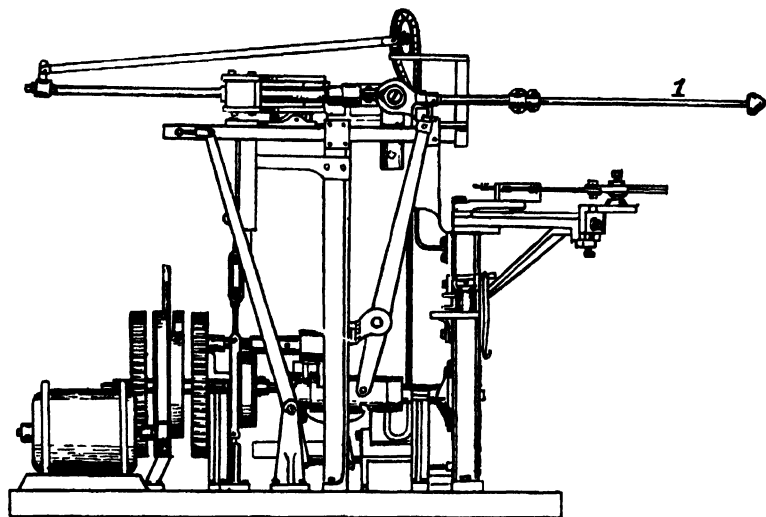


FIG. 194.—THE JENSEN AND HENLE FEEDER.

to the movements of a punty during hand gathering. In order to gather the glass the clay nose of the punty is advanced into the furnace, partly submerged in the molten glass, and rotated. During this gathering process the punty is pushed forward along the surface of the metal,

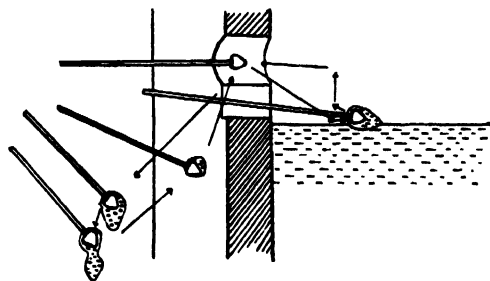


FIG. 195.—THE JENSEN AND HENLE FEEDER (PUNTY MOVEMENTS).

in order that the gathering may be localised at the forward end. Punty and gathering are now lifted, and at the same time drawn back slightly in order to form a tail and so allow the metal to enter the mould easily. This motion is succeeded by a slight sideways movement, by which, as the gathering breaks away from the surface of the metal, the broken

thread falls to one side of the gathering point, and the tendency to produce blisters and cords in succeeding gatherings is thus reduced. The punty is withdrawn rapidly from the furnace, swung over the delivery point, and lowered over the mould. Rotation of the punty is then stopped, the gathering flows off into the mould in the form of a gob, and is severed by shears. Finally, a rotation of the gathering iron through half a revolution brings the severed end of the residual glass to the top and the gathering process is then repeated. Fig. 195 indicates diagrammatically the motions of the punty through a complete cycle of the gathering operation.

(330) **The Owens Bottle Machine.**—The Owens automatic bottle machine (Fig. 196) is a continuous rotary machine, electrically driven, and consists of a number of arms or what are commonly known as "heads," supported by and located radially around a central shaft, mounted on a travelling frame or carriage. Each of the heads is a complete unit, and carries a finishing mould, parison mould, neck mould, and a plunger for forming the neck, the mechanical movements of the various component parts of each head being actuated by stationary cam paths on the fixed framework of the machine.

The central shaft and the projecting arms therefrom, supporting the heads, are hollow castings, and provided with outlets controlled by butterfly valves. Through these ducts air is circulated for cooling the moulds, the air being supplied by a high-pressure fan with a capacity of 12,000 cubic feet of free air per minute.

The machine is equipped with two motors, a 3 h.p. motor for raising and lowering for vertical adjustment and a 6 h.p. motor for driving, the actual power required being approximately 5 h.p.

There are six standard types of Owens machines, the "A" and "AE," having six heads, for medium small to medium large ware, the "AN" and "AR," ten-arm machines for small and large ware respectively, and the "AQ" and "AV," fifteen-arm machines, also for small and large ware respectively. In addition, special machines are built for the manufacture of large bottles such as Winchester quarts, etc.

The first type of this machine to be built was the six-arm, but it was soon found that on large orders for a particular bottle, where the additional mould expense was justified, a machine with a greater number of units or heads would make greater production possible, and it was therefore decided to build a machine with ten arms. After several years the same reason seemed to justify a still greater number of units per machine, and the fifteen-arm machine was accordingly built. There are, however, very few kinds of bottles used in sufficiently large quantities to justify the mould expense and operating difficulties of the fifteen-arm machine, and this size has not therefore been generally used. The ten-arm machine is the most economical size, although there are many orders of small quantities where the cost of manufacture is less on the six-arm machine than on the ten-arm machine.

OPERATION.—The machine operates adjacent to an auxiliary furnace, which furnace is composed of a combustion chamber over a revolving pot. The revolving pot is 10 feet in diameter and carries glass to a

depth of 8 inches, this being supplied or fed continuously from the refining tank of the melting furnace (see p. 378).

A portion of the revolving pot projects approximately 16 inches beyond the walls of the combustion chamber, exposing a segment of

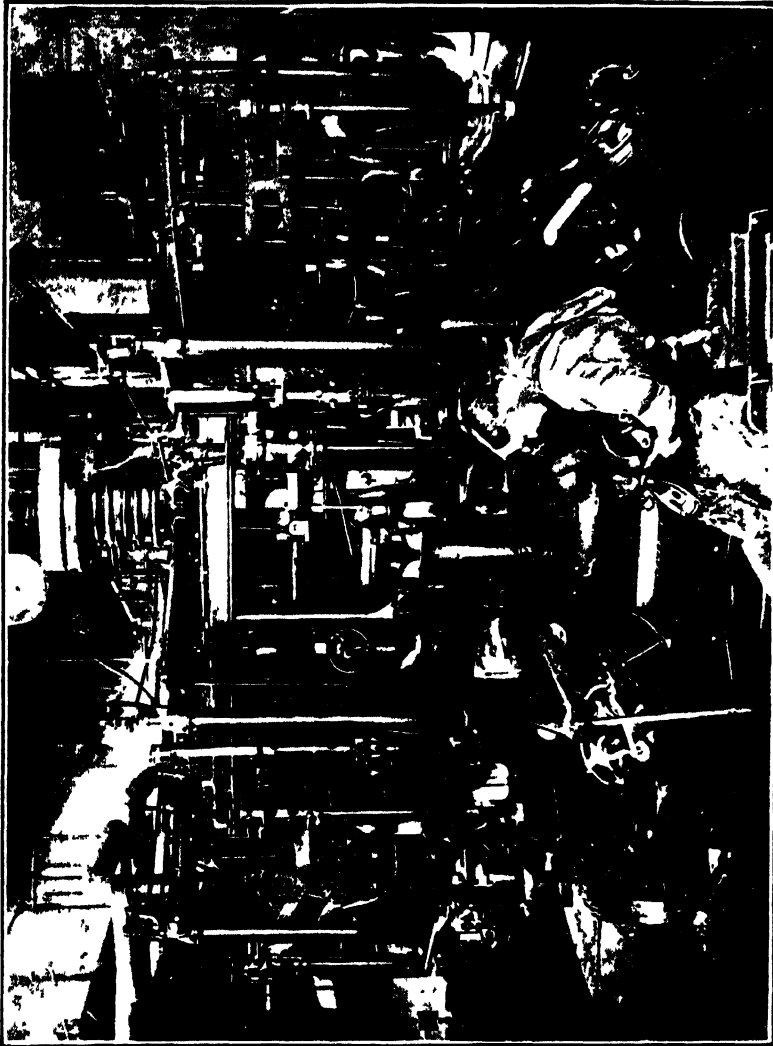


FIG. 196.—THE OWENS AUTOMATIC BOTTLE MACHINE
(By courtesy of the United Glass Bottle Manufacturers, Ltd., London, per
T. C. Moorshead, Esq., M.Am.Soc.C.E.)

the glass surface. The gathering moulds of the machine dip into this exposed molten glass consecutively as the machine rotates, and as each mould dips into the glass a vacuum is automatically created in the mould, sucking the glass up into it and thereby forming the parison (Fig. 197). The machine and the pot rotate in opposite angular directions, so that

over the small path in which the mould is dipping into the glass, the linear movements of the two are in the same direction, although the

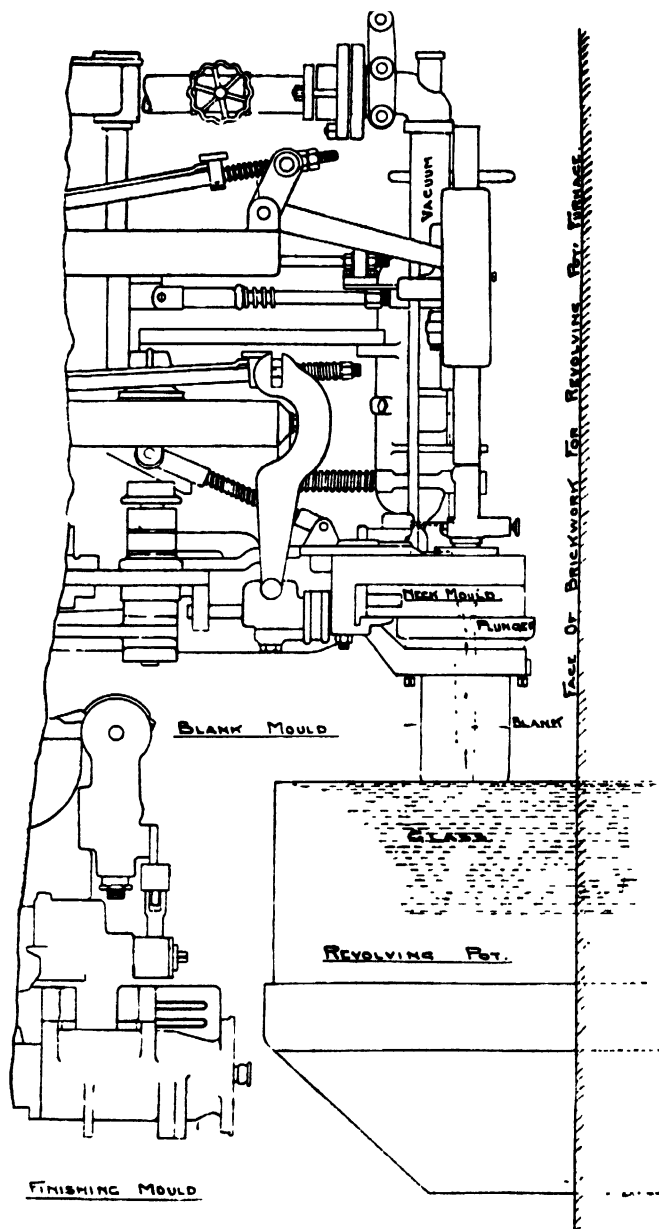


FIG 197.—THE OWENS MACHINE (PARISON FORMATION).

(By courtesy of the United Glass Bottle Manufacturers, Ltd., London, per T. C. Moorshead, Esq., M.Am.Soc.C.E.)

mould is travelling rather more rapidly than the glass beneath it, thus keeping in contact with hot unchilled glass.

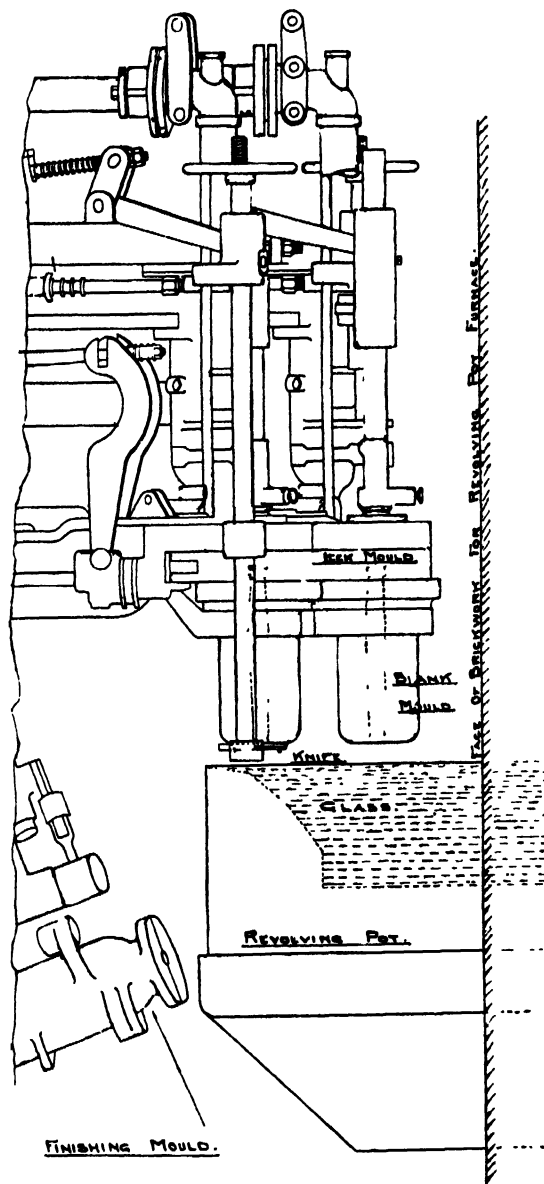


FIG. 198.—THE OWENS MACHINE (SHEARING DEVICE).

(By courtesy of the United Glass Bottle Manufacturers, Ltd., London, per
T. C. Moorshead, Esq., M.Am.Soc.C.E.)

As the mould rises up and moves away from the glass a knife automatically cuts off the string of glass which remains attached, dropping

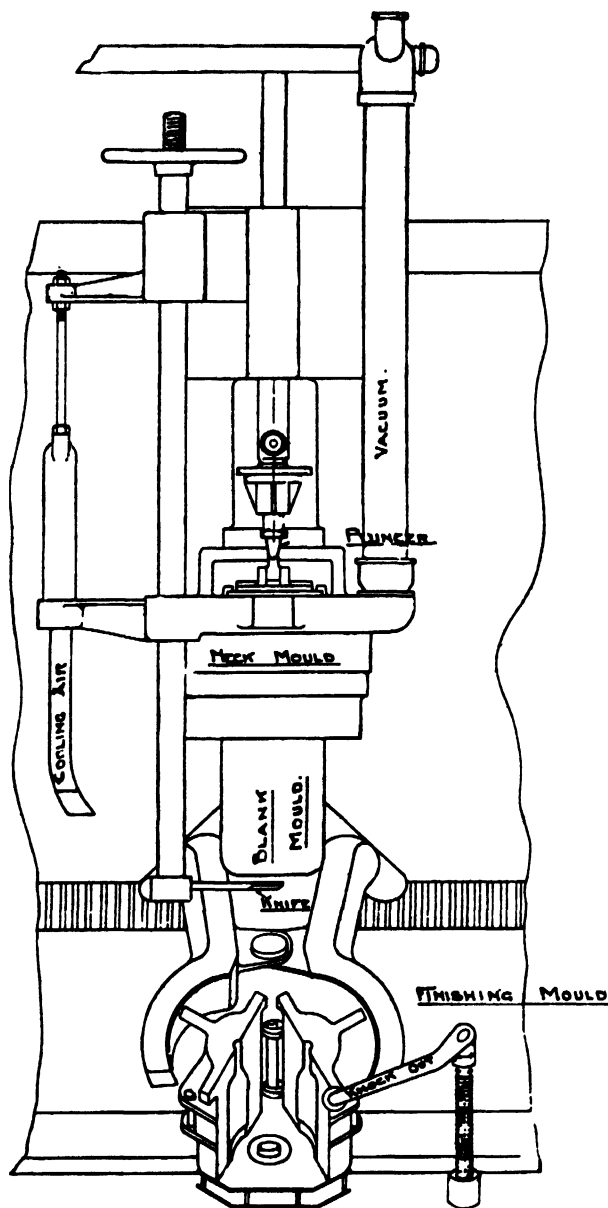


FIG 199.—THE OWENS MACHINE (KNOCK-OUT ARM).

(By courtesy of the United Glass Bottle Manufacturers, Ltd., London, per
T. C. Moorshead, Esq., M.Am.Soc.C.E.)

that portion not in the mould back into the furnace (Fig. 198). Whilst the knife is in position a slight puff of air consolidates the parison.

During the rotation of the machine the parison mould opens, leaving the parison exposed, suspended by the neck-ring mould.

The open finishing mould is situated at the extremity of a hinged arm, and rests upon small bearing rolls which run on a cam path. At the feeding position this track is so situated that the finishing mould arm hangs downwards and allows of clearance between the mould and the pot. Beyond this point the track slopes upwards, and the mould, in its rotation, is thus raised until it is on the level of the parison, which is at this stage freed from the parison mould. When the finishing mould has risen it is gradually closed by means of toggle arms actuated by rolls running on a second cam path, the operation being so adjusted that the closed mould now surrounds the parison.

Compressed air is admitted at this stage and the bottle is blown. The cam track once more dips, and the finishing mould descends, the two halves afterwards opening to free the finished bottle. The latter is prevented from falling by the action of a knock-out arm (Fig. 199), which moves over and holds the bottle upon the base-plate of the mould. At a further stage of the rotation, whilst the finishing mould is still depressed, the carrier passes a shaped receiving trough, and the knock-out arm moves outwards, so that the bottle falls off the mould base into the trough, and slides down on to a table for conveyance to the lehr.

There is an automatic oil-feeding system connected to and operated in conjunction with the machine, which system provides constant lubrication to all the vital bearings where these are subjected to extreme heating.

PRODUCTION.—The average possible production of various sizes of bottles on the Owens machine, for the various types of machines, is stated to be as indicated in Table C.

TABLE C.—PRODUCTION PER HOUR ON THE OWENS MACHINES.

<i>Capacity of Bottle.</i>	1 oz.	2 oz.	4 oz.	6 oz.	8 oz.	12 oz.	16 oz.
6-arm machine ..	—	—	1,300	1,300	1,200	1,000	900
10-arm ..	3,200	3,000	2,800	2,500	2,100	1,600	1,400
15-arm ..	4,200	4,000	3,700	3,500	3,000	2,200	2,000

There will, of course, be some little variation from the production figures given above, according to the shape and characteristics of the bottle, but it is claimed that these quantities represent the average number of marketable bottles that should be produced per hour for the sizes shown on the three different types of machines.

For certain kinds of bottles and on sizes below three ounces in capacity, much greater production than that shown in Table CI. is possible by means of what is commonly known as the plural mould operation.

This is where either two or three bottles are made at one time in one mould on each head, the mould being a compound of two or three single moulds, in which case it practically doubles or triples the figures given.

To illustrate this there was an actual case of a bottle of quarter-ounce capacity being made three in each mould on an **AN** type ten-arm machine. The machine operated at six revolutions per minute, and over a period of ten days' running actually produced an average of 10,080 marketable bottles per hour, or 1,680 gross per day.

CHAPTER XXXIII

THE MANIPULATION OF GLASS—*Continued*

III. Paste Mould and Pressed Ware Machines.

(331) **Paste Mould Machines.**—Simple cast-iron moulds give to the surface of the glass blown in them a rough, somewhat unpolished appearance, whilst in the case of divided moulds the line of junction is indicated on the finished glass by a ridge, the so-called "mould mark." As we shall see later, when discussing hollow-ware, these faults may be obviated by the use of wooden or carbonaceous moulds in which the parison is rapidly rotated as it is blown up to shape. The carbonaceous surface may be secured in a cast-iron mould by the application of "mould pastes." The composition of these pastes will be considered in detail in the hollow-ware section, and it may suffice to say here that the paste on coating and smoothing over with a hot gathering of glass leaves a homogeneous carbonised surface on the inside of the mould. Paste mould machines are designed to blow articles in paste-coated cast-iron moulds with a rotation of the glass during blowing. They have been developed more particularly for the production of electric lamp bulbs and similar thin-walled ware required in large quantities. Two machines widely employed for paste mould work are the Empire and Westlake machines.

(332) **The Empire Machine.**—This is a semi-automatic machine in which the metal is gathered by hand on a blowing iron, which is then placed in the machine. The marvering and blowing are performed automatically by the machine itself. The following brief description will indicate the mode of working of this machine.

Around a central vertical column rotates a drum, driven by a motor situated in the base beneath. Four rectangular frames, provided with rollers, are so placed as to bear upon the top and bottom edges of the rotating drum. These frames either remain stationary or rotate with the drum, as regulated by a clutch which is thrown in or out by means of an electro-magnet. The frames serve to hold the blowpipes when delivered, and for this purpose each is provided with a chuck rotated by gearing. There are three positions in each revolution of the carrying frames around the central column at which they come to rest—namely, (1) loading position, (2) elongating position, and (3) unloading position. At the loading position the blowpipe is placed horizontally in the frame, but as the latter commences to revolve the blowpipe nose is lifted somewhat and the parison is pressed and rolled against an arched marvering plate. The plate then swings away and the blowpipe is moved into a vertical position with the parison at its lower end. Mould sections attached by a rod to the carrier, and up to this point held below

in a water bath, now rise and close over the parison. The machine is provided with a special attachment, so that the carrier is brought to a standstill during elongation of the parison, but when this is complete the clutch is once more thrown in and the rotation around the column recommences.

Air under pressure is supplied from a chamber in the central column through a flexible pipe to the blowpipe chuck, and by means of a valve is admitted to the blowpipe for the required time for blowing, so shaping the glass. The carrier stops at the unloading station and the blowpipe is removed, after which the frame by further rotation arrives once more at the loading position.

(333) **The Westlake Bulb Machine.**—The Westlake machine (Fig. 200) is a completely automatic apparatus, giving very successful results in the manufacture of electric lamp bulbs. The glass used is a "semi-crystal" lead glass, and it is melted in closed pots in regeneratively heated furnaces. At first, the machine was supplied with glass from a two-mouthed pot, set in a special furnace, but it has been found possible to use a small tank furnace for this purpose. The machine is situated adjacent to a working opening at the side of the furnace, and the glass, as melted and fined, is ladled from the pots at regular intervals and in constant amounts, and placed in the tank through an opening in the side remote from the working point. Heating is performed by flames playing from end to end of the tank.

The machine itself consists of a series of units, each comprising (1) a gathering mould, (2) a spindle or blowpipe, and (3) a blow mould, each unit being mounted on framework rotating around a central stationary drum. Many of the operations of the machine are controlled by worm gears or pinions, bearing on segmental racks situated around the drum, a few by cam tracks and slides, the racks and cam tracks being so placed as to bring the devices into operation at precisely the times required. As with the Owens machine, gathering is performed by suction, but in this case the blank moulds are situated at the ends of long arms or rams, sliding on inclined supports in the upper part of the framework. On each ram is a rack, engaging with a pinion placed upon a shaft, which shaft is rotated by a second pinion and rack. By this means, when the ram reaches the front of the furnace, it is driven outwards and downwards, through the working opening and on to the surface of the glass. For convenience the rams enter the furnace in pairs, two blank moulds being filled at one time. In the older twelve-spindle machine the rams are freed from the rotating framework during the time of gathering, to commence revolving about the drum again when they are withdrawn from the furnace. Thus, before gathering, each ram takes up a position in advance of its spindle, the position being so regulated that when the ram retreats after gathering it is situated directly above the spindle. The newer machines possess twenty-four spindles, and gathering takes place without cessation of the rotary motion of the ram. In this case it is evident that the ram and spindle are situated in the same radial line during the whole of the rotation of the drum.

The blank mould is in the form of an inverted cup, with a hinged lid beneath, this latter being pierced with a central opening. Before

gathering, the lid closes, and glass is then sucked up through the opening into the cup. After filling, the mould is raised somewhat from the

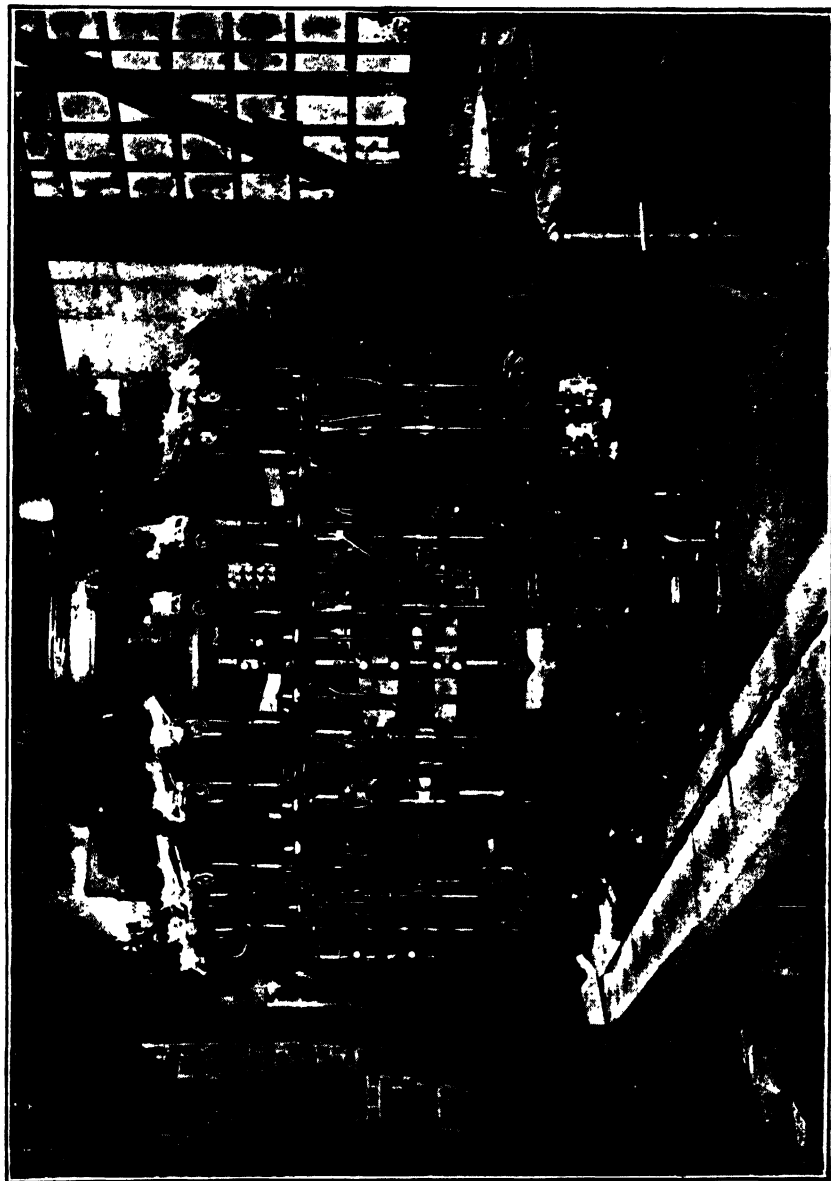


FIG. 200.—THE WESTLAKE BULB MACHINE.

(By courtesy of the Lemington Glass Works of the General Electric Co., and C. Wilson, Esq.)

surface of the glass and a knife sweeps below it, cutting off the glass thread. The ram then retreats until the gathering cup is directly over the nose of the blowing spindle.

Attached to the nose of the blowpipe is a pair of small pivoted jaws, which are open at this stage. The cover of the blank mould now opens, the charge drops on to the nose of the blowpipe, and it is then held securely by the closing of the jaws. Inside the pipe is a plunger, which now ascends and presses a small hollow in the glass. Within the plunger is a longitudinal air passage with a duct leading to grooves on the plunger face, and by this means a small amount of air is admitted to the parison to assist in shaping.

Each pair of blowing spindles is held in a yoke, and this yoke can be rotated by a spiral pinion and rack, actuated by a stationary cam. As we have seen, when the charge of glass is received the blowpipe is vertical, nose upwards, but it then rotates, in two stages, until the pipe is again vertical but with the nose below. At the first pause, when the pipe is almost horizontal, and again when it is vertical, the pipe is given a spinning motion around its long axis, and this ensures an even bulb.

In the older machines elongation of the parison, which occurs at the stage when the pipe is once more vertical, was accomplished by imparting to the pipe a swinging motion, similar to that which would be given by

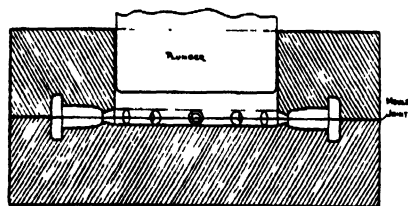


FIG. 201.—A STOPPER MOULD

(By courtesy of C. C. White, Esq., Messrs. Peter Waddington and Sons, Ltd.,
Mexborough.)

a human blower. In machines with twenty-four units lack of space prevents this motion, and elongation is accomplished with the accompaniment of the spinning motion only.

Blow moulds of the paste-mould variety are used, and each is mounted on a movable arm. During the above period the mould has been held down in a water trough for cooling. When the parison has been elongated the mould is raised and closes over it. Air is then admitted in suitable amount into the pipe and the bulb is blown.

Throughout the blowing process the rotational motion of the pipe is continued, so that no mould marks are left on the finished bulb. Finally, the blow mould opens, the bulb is released from the iron by the opening of the jaws, and drops on to a conveyer belt, whilst the mould once again descends into the trough.

Meanwhile, in the twelve-unit machine the parison mould, after delivering its charge, moves again to its advanced position, and there remains under a jet of cooling air until the furnace opening is once more reached. In the twenty-four-unit machine a cooling pipe moves into position under the parison mould after the charge has been delivered.

The twenty-four-unit Westlake machines are stated to produce two thousand or more bulbs per hour.

(334) **Machines for Pressed Ware.**—Although relatively simple in design, press machines are of more recent origin than narrow-neck bottle-

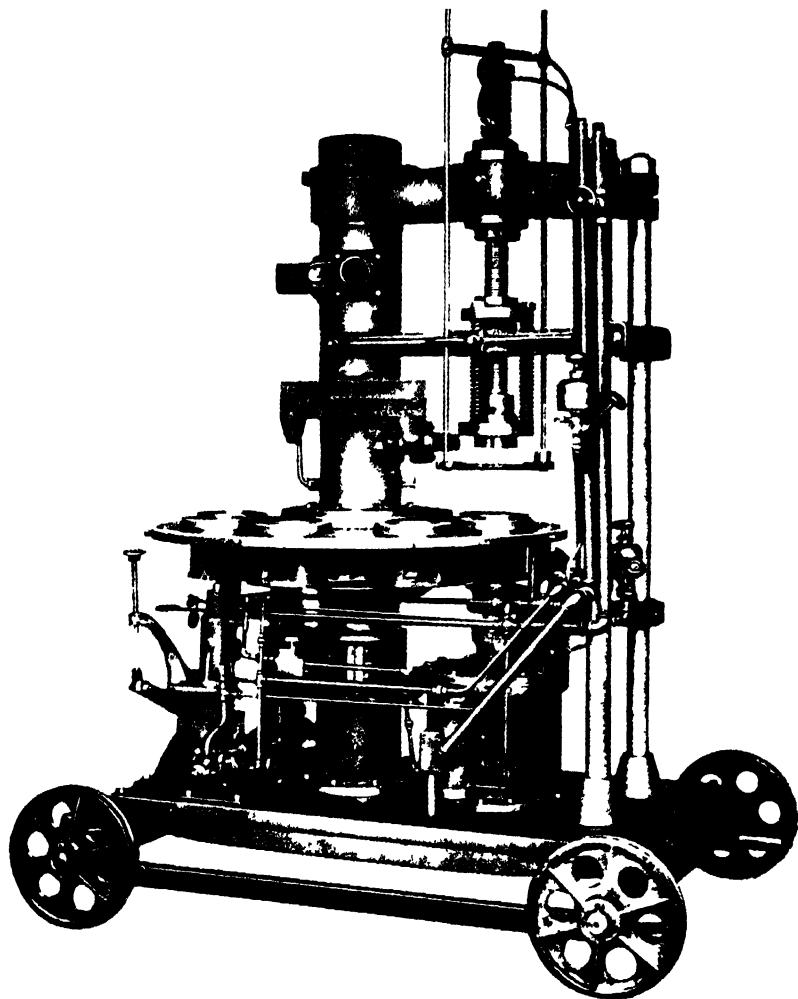


FIG. 202.—THE E. MILLER PRESSING MACHINE.

(By courtesy of the Miller Machine and Mold Works, Columbus, Ohio.)

forming machines. They are now used extensively for making stoppers, hollow-ware such as tumblers, jars, etc., and even for such complicated articles as basins with stem and foot. They are generally of the side-lever type, approximating to the parison-forming portion of the simple

wide-mouth bottle blowing machines. The mould is shaped to produce the outer contour of the article to be made, and, for hollow-ware, the plunger shapes the inside of the vessel.

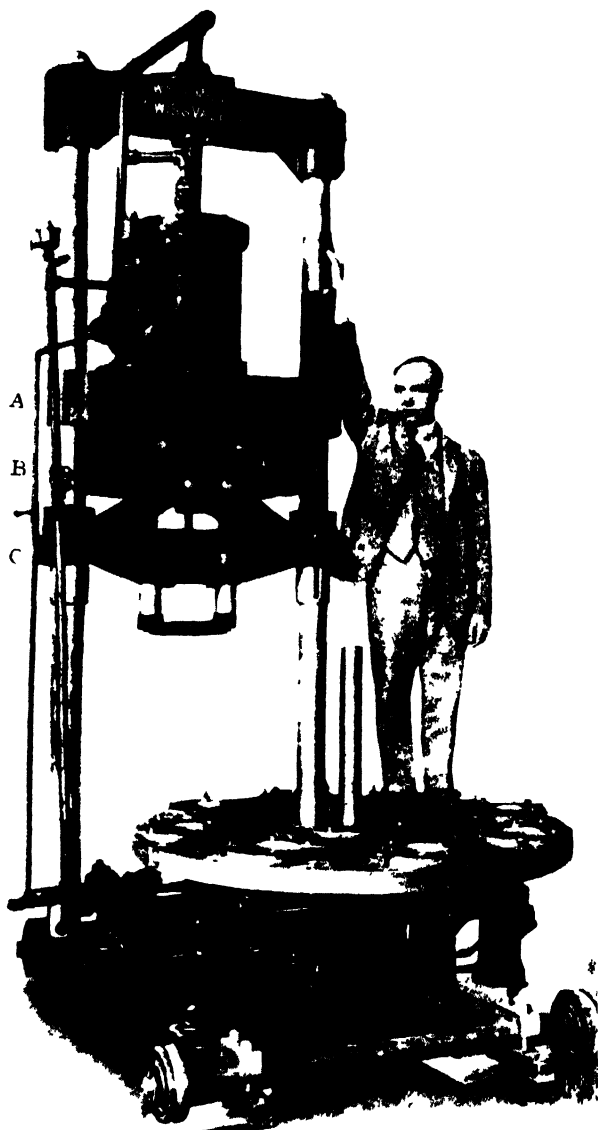


FIG. 203.—THE W. J. MILLER (MODEL AA) PRESSING MACHINE.
(By courtesy of W. J. Miller, Swissvale, Pa., per S. H. Rylett, London.)

In the case of the manufacture of small stoppers, multiple stopper moulds are used. The mould often consists of a central cylindrical opening, into which the plunger fits, surrounded by radially situated recesses of the shape of the stopper (see Fig. 201). Excess of glass is dropped into the central opening and the plunger is depressed, so squeezing glass into the recesses, from which air can readily escape along the mould joints. On opening the mould, the stoppers are seen to be radiating from a central plate of glass, from which they are afterwards broken. The severed ends of the stoppers are ground smooth on a wheel, whilst the central plate is returned to the furnace as cullet.

Automatic press machines are now made, in which the plunger is pneumatically depressed into the mould. These machines are useful for rapid working, and in this case a single plunger serves a number of moulds. An eight-mould machine of this kind, made by **E. Miller**, is illustrated in Fig. 202. The moulds are situated around a circular table and come beneath the plunger in turn as the table rotates. Depression of the plunger is secured by a piston-head situated in a framework above the table, and this piston is worked by compressed air. Production by this machine is given at from 25 to 36 articles per minute, and an automatic feeding device may be employed in connection with it.

A somewhat novel form of press machine, the patent of **W. J. Miller** (Model **AA**), is shown in Fig. 203. Instead of the usual form of plunger the piston is connected indirectly to the plunger through a toggle joint. During the operation the upper crosshead, **A**, remains fixed, and to this one end of each of the toggles is attached. The plunger in its descent forces down the cross connecting link, **B**, so driving apart the toggles and, through these, forcing downwards the movable head **C**. Such an arrangement multiplies the power of the stroke, and it is claimed that it would require a direct acting cylinder from 16 to 32 times as large to develop the same power. In addition, the plunger is driven with gradually increasing power as the stroke progresses, so meeting the gradually increasing resistance of the glass. Again, it is evident that a gathering light in weight requires more pressure to fill the mould than a heavy gathering. With this machine the smaller the gathering, the further the plunger penetrates, and consequently the greater the pressure due to the toggles, conditions not attained in the directly driven plunger.

CHAPTER XXXIV

THE MANIPULATION OF GLASS—*Continued*

IV. Sheet Glass.

(335) **Hand Methods of Production.**—Window glass is of two distinct varieties—firstly, sheet glass, made either in the form of cylinders or thin sheets drawn directly from the furnace, and secondly, plate glass. In this chapter we shall discuss the production of the former type, leaving the latter for subsequent treatment.

Although much sheet glass is now mechanically made, the old hand methods still exist, despite the fact that they are threatened before long with complete extinction. These hand methods of working show some variation in different districts. The use of open pots for melting, placed in rectangular furnaces, is still adhered to in some parts of Europe, and the furnaces used generally contain six to ten pots. Melting and fining of the glass is accomplished in 30 to 36 hours, and the pots are worked out in 12 hours. For reheating the large parisons of glass during working it is usual to have special glory-holes at the front of the furnace, accessible from the working benches. These glory-holes are large enough to contain the cylinders when blown, and are heated by means of special flues leading from the main gas flue of the furnace. It is necessary to maintain the temperature of the glory-holes as high as that of the furnace, and for this reason they must be lit two or three hours before working out commences. They possess an opening 28 to 32 inches wide to allow of the admission of the cylinders, which opening can be partially closed by a movable partition, in order to protect the worker from heat radiated from the chamber. In the centre of the long side of the partition is a semicircular opening, provided with a hook for the support of the pipe when the parison is to be rotated in the glory-hole. Along both sides of the furnace in which the glass is melted run stout wooden platforms, sometimes partitioned off by short walls into working compartments, in which case the walls also serve to brace the furnace. At the edge of the platform near to each working hole is a smooth iron marvering slab and a water trough. Against the latter is a post surmounted by an iron fork for supporting the pipe during the working of the glass, the hot pipe so projecting over the water that it may be readily cooled whenever necessary. A large oak block, suitably hollowed, and containing a number of cavities, is also provided for shaping the parison. It is evident that this block must be cooled whilst in contact with the hot glass, or burning and consequent loss of shape would result, and cooling is accomplished by ladling water into the many cavities in the wood before use. In some works the wooden block is replaced by a

shaped iron slab, but in such cases this must be covered with moist shavings or a similar protection before use to prevent the glass from sticking to the iron when it becomes heated.

Against the platform is a hole or pit of sufficient size and depth to allow the cylinders to be swung therein during elongation (*see* Fig. 126).

Where tank furnaces are used these may be of almost any type, either simple or divided. Tanks possessing dividing walls and bridges are most easily regulated, thus finding most favour. In some cases the tank is divided into three chambers, for melting, fining, and working respectively, more often into two. One common practice is to divide the tank above the liquid by brick screens, below which are merely placed floating bridges. For tank furnace practice no glory-holes are required, for the glass is reheated in the working holes without any serious loss of temperature of the furnace itself or consequent chilling of the metal it contains. As for the tools used with tanks, they do not differ materially from those described above for pot furnace work.

Pot furnaces are still used to some extent in France and Germany, whilst in Belgium, England, and America tanks find almost universal employment.

The actual process of making cylinders can best be explained by considering in detail the different methods employed.

(336) **The Franco-German Method.**—In this process the length of the cylinder blown corresponds to the length of the sheet of glass desired and its circumference to the breadth of the sheet. It is possible in this way to obtain sheets 2.6 metres long by 1.1 metres broad without undue exertion. The pipe employed is of the usual type, except that it possesses a rather large nose-piece. To commence the process the nose of the pipe is dipped into the glass, rotated once or twice, and, having so gathered a small amount of glass, withdrawn.

Rolling and pressing on the marver, coupled with gentle blowing, now serves to shape the gather into a small sphere. When the metal is sufficiently cool it is again dipped into the glass and rotated, whereby a second gathering is obtained. The shaping of the glass is now accomplished by rotating the pipe as it rests upon the post and suitably moulding with a wooden shaping tool, kept moist by occasionally dipping it in the water. During this process suitable blowing helps to give the glass the required shape. When the glass is sufficiently set a third gathering is made, this being usually sufficient for small cylinders, but where large sheets of glass are to be made, up to five gatherings are often necessary, each successive one being treated as the second.

An assistant next takes the pipe and, by rotating it in the fork and also shaping the glass upon the special wooden block, obtains a parison, of the shape first shown in Fig. 204, *a*, and then as in Fig. 204, *b*. The thin upper wall close to the pipe has now chilled sufficiently to retain its shape, and this determines the diameter of the cylinder. On the other hand, the lower part of the wall is still thick, and remains fairly soft. The parison is now partly introduced into the glory-hole, so that the thicker portion only is heated, the pipe being rested upon the hook in the partition and rotated.

When the heated portion is sufficiently softened, the whole is rapidly

withdrawn, the pipe held vertically over the pit, and by a swinging pendulum-like motion, the parison is caused to elongate, partly under its own weight and partly due to strong blowing down the pipe. By this means a cylinder with a wall of even thickness is obtained. Should the lower portion of the cylinder have cooled before the parison is of

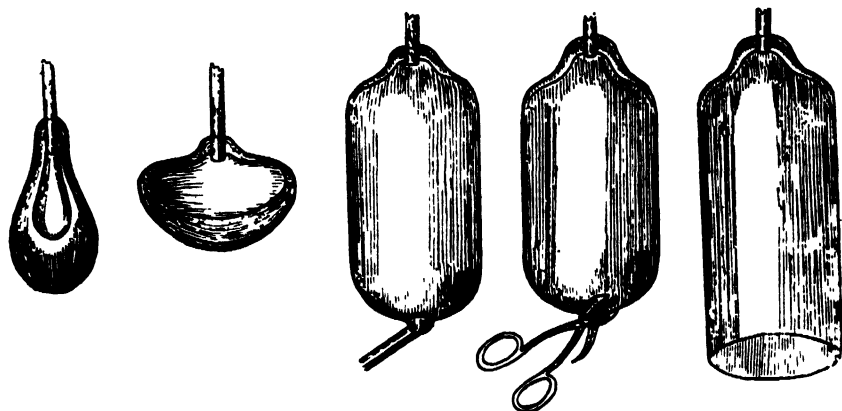


FIG. 204.—THE HAND PRODUCTION OF SHEET GLASS: FRANCO-GERMAN METHOD.

sufficient length it is again heated in the glory-hole and the swinging process repeated. The cylinder now presents the appearance shown in Fig. 204, *c*, and the next step consists in opening the end. For this purpose a rod is dipped into the pot, the small gathering of hot glass so obtained being brought against the centre of the closed end of the

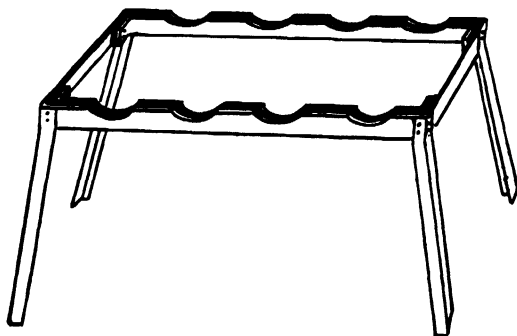


FIG. 205.—A "CRACKING-OFF" STAND.

cylinder, whereby the glass is softened at this point. The cylinder is now rapidly thrust into the glory-hole and the pipe closed with the hand. By this means enclosed air is heated, expands, and blows a small hole in the end of the cylinder where the glass is soft. The glass is once again removed, rested upon the fork, and an assistant enlarges the hole so

obtained by a pair of shears (Fig. 204, *d*). Again is the glass heated in the glory-hole, with slow rotation, until, when red hot, it is rapidly withdrawn and swung in the pit, when the lower end opens out to the same diameter as the rest of the cylinder (Fig. 204, *e*). The blowing is now completed, the cylinder is laid upon a special stand (Fig. 205), the glass close to the pipe touched with a cold iron, and the pipe freed and removed by striking it a sharp blow.

(337) **The Bohemian and German Method.**—In this process the length of the cylinder corresponds to the breadth of the glass sheet, its circumference to the length. Since it is easier to enlarge the cylinder lengthways by gravity, as in the French method, than diametrically, which latter can only be accomplished by blowing, it is natural that the Bohemian method fails to produce such large sheets as are made by the former process; sheets little more than one metre square are about the limiting size. The process is somewhat similar in operation to the one just described. The assistant warms the nose of the pipe and gathers some metal from the surface of the glass. Care has to be taken that the pipe does not touch the ring or dip too deeply into the metal during

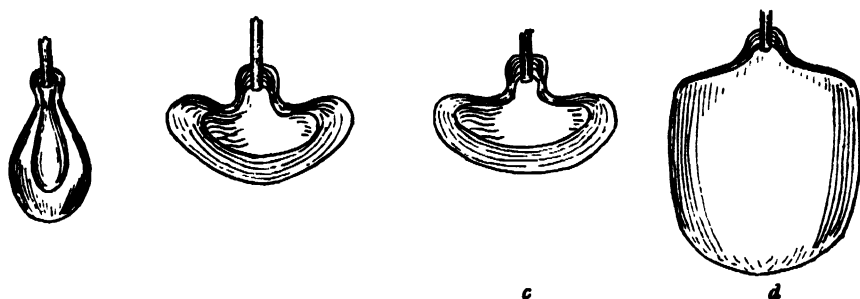


FIG. 206.—THE HAND PRODUCTION OF SHEET GLASS: BOHEMIAN AND GERMAN METHOD.

gathering, since impurities result in the former case and seedy metal in the latter. The pipe is now rested upon the supporting fork and rotated until the metal is sufficiently set to remain upon it. At the same time a small cavity is blown into the glass. The gathering and manipulation is repeated until sufficient glass has been obtained, whilst a special iron shaping tool is used to round the parison during rotation. At this stage, by means of the tool, glass is driven forward from the nose of the pipe until a ring-shaped hollow is formed, where, later, the cracking off takes place, the glass having then the shape indicated in Fig. 206, *a*. Save for a small cavity at the nose of the pipe, the parison is a solid mass of glass.

The next process consists of warming the glass at the glory-hole or working hole, and shaping it by rotating on the wooden shaping block, accompanied by suitable blowing, until the diameter of the shoulder is that of the cylinder to be made. It is necessary, in blowing big cylinders, to arrange, during gathering and shaping, to work sufficient glass into the neck to support the cylinder in the latter stages of the

process. The pipe is now held overhead and, by powerful blowing, a parison of the shape indicated in Fig. 206, *b* is formed. The pipe is rapidly dropped, giving the shape shown in Fig. 206, *c*. Further heating at the glory-hole, with rotation in order to retain the shape until the bottom of the parison is sufficiently hot, then allows of the elongation of the cylinder by swinging in the pit, accompanied by blowing. The shape of the parison after elongation is as shown in Fig. 206, *d*. In the case of thin cylinders much air is next blown in, the pipe closed with the thumb, and the parison strongly heated, whereby the whole assumes a cylindrical shape through pressure of the internal expanding air, whilst when the end is sufficiently soft it is burst open by the same means. Rapid rotation of the pipe as it rests in the support now serves to open the end further until it is uniform in diameter.

In cylinders of 30 to 40 cm. in diameter, the cylindrical end when opened and expanded would not be sufficiently thick-walled, so that with such cylinders a gathering of glass is placed upon the dome-shaped end and evenly spread by an iron, before the end is burst open, the

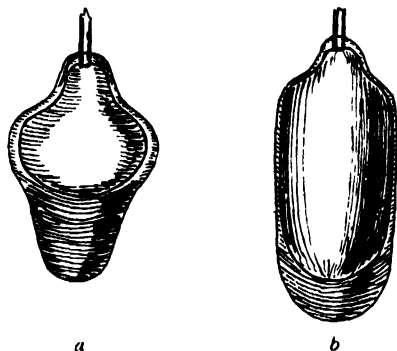


FIG. 207.—THE HAND PRODUCTION OF SHEET GLASS: BELGIAN METHOD.

cylinder being finally swung again to make the glass uniform. If the glass is unevenly spread the edge is so cut with shears that by reheating and rapid rotation the desired shape and thickness is obtained. The blowing is now finished.

(338) **The English, Belgian, and American Methods.**—These differ but little in detail from the previously described Franco-German process, with, of course, the previously noted exception of the extensive use of tank furnaces and the elimination of glory-holes.

In Belgium extremely long cylinders are generally blown, and the method of manipulation is somewhat distinctive. The parison is first worked into a shape as shown in Fig. 207, *a*; then, by placing the pipe on the fork in a sloping position and rotating it rapidly, accompanied by strong blowing, the shape assumed is as Fig. 207, *b*. Swinging now serves to elongate as described above.

Hand methods in America had almost died out until the exigencies of war-time called for a largely increased production of window glass. At present somewhere about one-third of the window glass made in the

United States is hand-made, but the proportion, as in all countries, is likely to decrease rapidly due to the advancement of more rapid and economical machine processes.

(339) **Blown Plate Glass.**—Small plates of glass are made by the hand process in the same way as sheet glass. When large plates are needed, however, the process becomes more difficult. Large quantities of glass up to 110 lb. are required, the shaping of such parisons being extremely laborious. The swinging of the pipe is achieved by attaching it to a chain for support. To open the cylinder it is heated at the end and a pointed iron tool driven through, by which means a hole about 5 cms in diameter is formed. On reheating, the hole is enlarged with shears until it is of the diameter of the cylinder. The springing of these cylinders is also performed differently from that of sheet glass, the cylinder being cut open with shears from each end to the centre in turn.

(340) **Opening the Cylinders.**—For cracking off the neck of the cylinder two methods are available. If the walls are thin it is sufficient to draw a thread of hot glass and wrap it around the desired point, when at once, or on touching the glass with the moist finger, a clean crack is obtained. In the case of thicker glass, an iron tool of the shape in Fig. 208 is heated and drawn around the shoulder, followed by a drop of water, when the desired result ensues.

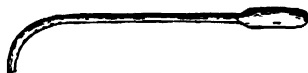


FIG. 208.—A TOOL FOR CYLINDER SPLITTING.

As a preliminary to flattening, the cylinders must be sprung open lengthways. This springing is performed from within. The short and wide cylinders obtained by the German method are cut by means of a diamond, and when opened, small wedges of wood are placed at each end to prevent the severed parts from springing together. These wedges later burn away in the flattening oven. The long Belgian cylinders are cut by means of a long red-hot iron drawn along the inside of the cylinder.

(341) **Flattening Ovens.**—In order to flatten out the cylinder after springing open it must be introduced into a special furnace, heated sufficiently to soften, then stroked down upon a smooth, flat fireclay slab until it is quite flat, after which it is slowly cooled to anneal.

The most common type of flattening oven employed in Europe is that designed by Biévez. A simple older form is illustrated in Fig. 209, and is used as follows: Two gas-heated chambers, **A** and **B**, are provided for flattening the glass, whilst between these lies the cooling Lehr, **C. L.** Entrance flues, **F₁**, serve to conduct the heating gases to the chambers, whilst exit flues, **F₂**, serve to remove waste gases. Running completely across from **A** to **B** is a rail track on which are two waggons, and on each of these lies a flattening stone. The cylinder is gradually warmed as it passes through the entrance channel, **D**, and it is then passed forward on to the stone situated in **A**. Standing at the opening, **H₁**, the workman waits until the cylinder begins to fall, and then, if necessary, presses down the two halves with an iron paddle, causing the sheet to lie, though

somewhat unevenly, upon the stone. A flattening tool is now introduced, consisting of a block of wood, clean and free from knots, attached to an iron handle. With the wood the glass is now smoothed until it is, as far as possible, plane. During this time the second waggon stands in chamber **C**. When the glass is sufficiently flattened the waggon in **A** is pushed along into **C** and so drives the second waggon into **B**. Then from channel **D**, a second cylinder is taken, placed on the stone in **B**, and similarly flattened. By the time this is completed the sheet in **C** is somewhat chilled. It is now passed into the lehr passage, **L**, by a stout rod inserted through the hole, **O**. Along the lehr runs an iron framework, consisting of a number of rods, bolted to a crossbar at the open end, **P**, and sunk in channels running the length of the lehr. At regular intervals,

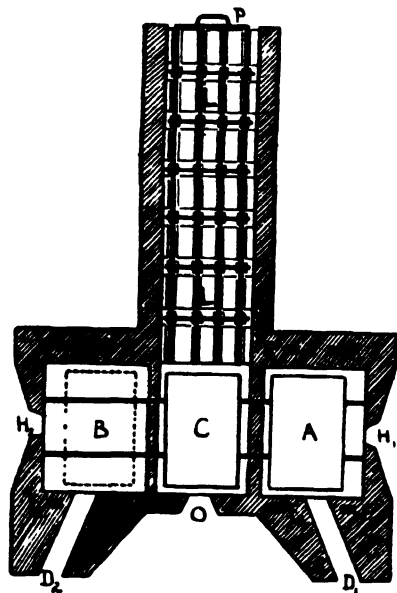


FIG. 209.—A FLATTENING OVEN (OLD TYPE).

sunk in cross-channels, are shafts upon which rollers are mounted, these rollers serving to support the iron bars lying above them. By means of a lever, the whole of the cross-shafts can be raised just sufficiently to lift the framework a few millimetres above the floor of the lehr, whilst on release they allow it to sink slightly below floor-level. When the cylinder from **B** has been pushed into chamber **C** and a third cylinder flattened in **A**, the sheet lying in **L** is removed down the lehr a sufficient distance to allow the second one in **C** to take its place. The movement down the lehr is obtained by raising the framework above floor-level, thus raising the sheet slightly, and drawing the whole of the required distance along by means of the handle at **P**. By sinking the frame, it can now be driven back into its original position without disturbing the glass above it. Successive movements serve to introduce a series

of flattened cylinders into the lehr and eventually deliver them at the far end.

Figs. 210 and 211 show a more recent type of flattening oven. Here a single flattening chamber, 1, is provided, whilst 2, the so-called "reversal chamber," is wide enough to hold three waggons side by side. Beyond the reversal chamber is the chamber 3, from which the flattened sheets

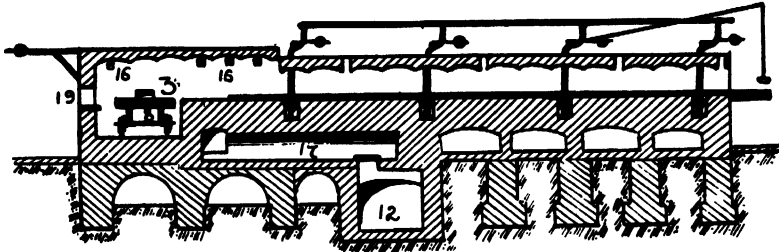


FIG. 210.—A FLATTENING OVEN (NEW TYPE).

can be introduced into the lehr. In chambers 1 and 3 are mounted rails for waggons, whilst in 2, at a lower level, are cross-rails upon which is placed a reversal waggon or bogie, 4. The latter is about two-thirds the length of the chamber, and upon it are bolted two pairs of rails, each of which, by suitably moving the waggon, can be brought into line with the rails in 1 and 3. A shaft projecting through the wall of the chamber allows of the adjustment of the reversal waggon to any desired position

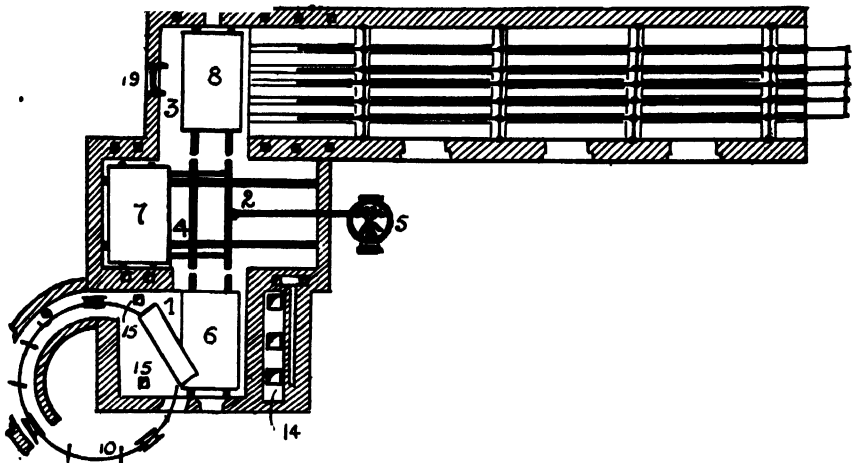


FIG. 211.—A FLATTENING OVEN (NEW TYPE).

by means of the rack and pinion 5. It is thus possible to receive a flattening waggon from either of the chambers 1 or 3, and transfer it to either the right- or left-hand recess in chamber 2. In the oven are three waggons, 6, 7, 8, upon each of which is a flattening stone. Cylinders

enter the oven by the curved passage **9**. Running along this preheating passage is a portion of the sheet-iron ring **10**, which itself rests upon three wheels, revolving in cast-iron supports. The ring contains three pairs of semicircular arms, and can accommodate three cylinders at a time. Each cylinder is mounted on the supports at a point outside the furnace, and, by a rotation of the ring, passes successively through the preheating passage into the flattening chamber, and is there laid upon a flattening waggon waiting to receive it. The ring is rotated by an assistant, who seizes it with a special iron key and pulls it around as desired. Heating gases pass from the main flue **12** through the secondary flues and burn at ports, **14**, placed vertically in a side pocket of the flattening chamber, or at smaller ports, **15**. The position of the ports gives a spread to the flame and ensures even heating of both the flattening chamber and of the preheating passage, **9**. These preheating passages are of doubtful advantage, often being dispensed with. A number of small ports, **16**, placed just under the roof and supplied from a flue, **17**, leading from the main flue under the lehr, maintain the temperature of the rest of the oven. It is usual to keep the temperature of the flattening chamber at 650° to 700° C., that of the reversing chamber at a point over the stones at 530° C. and the lehr chamber at 460° C., with a drop to normal temperature along the lehr. Although waste-gas flues connected with a chimney are sometimes provided, it is more usual to allow the products of combustion to pass directly into the factory through the various working holes, since this is held to prevent the presence of cold air currents and the consequent endangering of the sheets. In practice the following method is that adopted for opening the cylinder. After it has passed through the preheating chamber the glass is laid upon the waggon **6** and flattened as has before been described. The waggon is then pushed into chamber **2** and the reversing waggon moved so that the glass sheet now lies in recess **18**, whilst waggon **7** is now pulled into the flattening chamber and waggon **8** into the middle of the reversing chamber. A second cylinder is received and opened, during which time the first sheet is cooling somewhat. By returning the reversing waggon to its original position the waggon **6** can now be pulled into chamber **3**, then by a rod inserted through aperture **19** the sheet is pushed along into the lehr itself. By this means each sheet of glass spends an appreciable time in chamber **2** and the rate of cooling is diminished, whilst the empty waggon is not suddenly heated up by a rapid passage from lehr to flattening chamber.

In spite of these precautions, it will be seen that the flattening stone undergoes fairly severe variations of temperature. Further than this, since the waggons are wholly contained in the heated chambers, as also are the rails, they become somewhat warped and twisted in the course of time, and their movement entails considerable shaking of the stones. Since it is essential to keep the latter as smooth as possible and to prevent cracking and splitting of the surface, they cannot be prepared from refractory materials in the ordinary way. The slabs are of fireclay, of a surface area approximately 225 by 160 cm. The lower part of the stone is made from a mixture of from five to eight parts of coarse grog with two to three parts of plastic binding clay, whilst the upper portion,

although similarly constituted, has a finely ground grog, whilst to it, also, graphite may be added.

In forming the slabs a wooden frame is used, the surface of the clay being smoothed and polished. Drying is performed slowly, with great care, after which the slabs are very gradually heated in the pot-arch and are then thoroughly burnt. A final smoothing and polishing is now performed in the following way. The surface of the stone is ground perfectly flat with sandstone, and the slab is then painted over with a weak water-glass solution, which is rubbed in thoroughly to fill all the pores, and then allowed to harden. Again the surface is ground smooth with sandstone, and a second water-glass coating is applied, this containing some raw clay and dust grog. After a further period of hardening the surface film is ground down, just enough to give a polished surface on the slab, and a third coating of water-glass and finest sand is applied. When the last coat has hardened it is polished, first with soft sandstone, finally with talc, barytes, and dust grog, or a similar polishing material.

The flattening oven with separate stones has been largely replaced in America by a circular flattening oven with a revolving table supporting the stones. The oven is divided into quadrants, in the first of which the cylinder is laid and flattened. The table then revolves, until, as the sheet reaches the third quadrant, it is pushed into the lehr. This system allows of easy working and control, and also entails less shaking and jarring of the stones than the foregoing method.

(342) **After-Treatment.**—As the sheets emerge from the lehr they are dipped in a tank, of suitable length and depth, and a width of 25 cm., containing dilute hydrochloric acid, after which they are washed and reared up to dry. The dried sheets are finally sent to the cutting or packing rooms. During the splitting of the cylinders all faulty parts are marked and the splitting is arranged to bring all such regions as near as possible to the edge of the glass. The difficulties of cutting the flattened sheets so as to ensure as large an area of good glass as possible are thus minimised.

Although sheet glass obtained from cylinders is fairly good for most ordinary glazing, it is never free from small waves and irregularities, and windows from it always show some distortion. For the best work it can never equal or replace plate glass, although the higher price of the latter limits its use when cost is a prime consideration.

(343) **Machine-Drawing Processes.**—The foregoing methods of making sheet glass are not only laborious but give a product liable to many faults, whilst the size of the sheets is limited. It is natural, then, that the idea of producing glass by machinery in longer lengths than could be obtained by hand working should have been early conceived. We have noted previously an attempt by William Clark, of Pittsburg, whose process was patented in England in 1857. The idea was simple. It was, in fact, to dip into the glass a "bait" to which the glass would attach itself, and gradually withdraw this from the molten glass. By suitably regulating the speed of withdrawal with regard to the rate of the setting of the glass it was found possible to obtain a continuous sheet.

The method had one fault, but this was so serious that it baffled

a number of workers, and half a century passed before it was overcome and a commercially successful process evolved. The difficulty is that when a sheet of glass is so drawn, the second stratum is somewhat shorter than the first, the third is less still, and so on, so that, instead of a parallel sided sheet being formed, the two bounding edges approach each other and a triangular sheet is obtained (see Fig. 212). To overcome the defect several workers, of whom Greenhough and Picard may be mentioned, have tried the method of drawing the sheet downwards, that is,

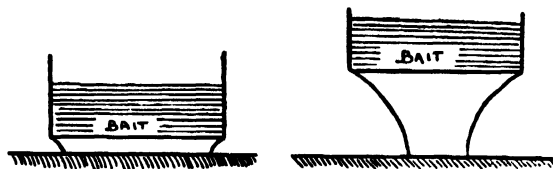


FIG. 212.—CLARK'S METHOD OF DRAWING SHEET GLASS.

by allowing the glass to flow through a slit of suitable size. Again a difficulty occurred, for as the sheet became heavier, the weight drew thinner the portion not yet set, and finally rupture was caused at a point more or less removed from the outlet. Instead of drawing with constant velocity a uniformly accelerated motion was employed. It was then found necessary to support the glass as it emerged from the slit between two rollers in order to allow of its regular descent. This caused a loss of transparency of the finished sheet common to all rolling methods.

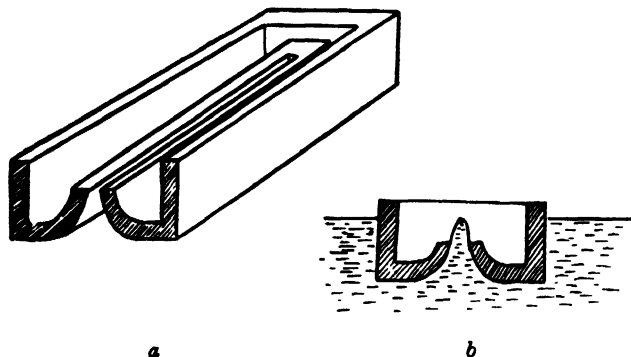


FIG. 213.—THE FOURCAULT PROCESS: FLOATING TROUGH.

Hanrez and Simon tried the method of drawing the sheets horizontally, supporting the glass upon a horizontal table, but again with notable loss of transparency.

(344) **Fourcault's Method.**—The first success in the process of drawing flat sheets was obtained by E. Fourcault of Belgium, whose method, as in the case of Clark, consisted in drawing the sheets vertically from a tank. Narrowing of the sheet of glass is caused by the overcoming of

surface tension of the sheet by the gravitational pull upon the molecules. If the liquid be given an upward velocity at the drawing-point in order to counteract the gravitational tendency the uniform width of the sheet will be maintained. In order to produce the upward movement Fourcault uses a float, a long trough of refractory material having, along its base, a slit parallel to the length of the trough (Fig. 213, *a*). The trough is caused to sink somewhat in the glass, and by two U-shaped arms the depth of penetration can be adjusted. Glass is therefore forced through the slit at any desired rate (Fig. 213, *b*). If so left, the glass would fill the inside of the trough to the level of the liquid outside. This, however, is prevented by seizing the glass as it emerges from the opening by means

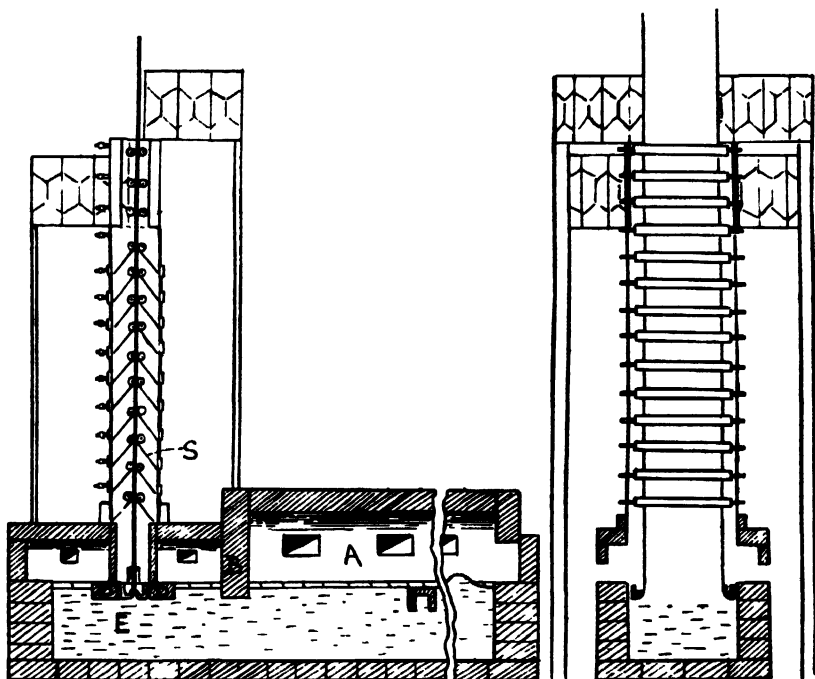


FIG. 214.—THE FOURCAULT PROCESS: GENERAL OUTLINE.

of a bait and drawing it off in sheet form. The trough, by its weight, is thus constantly forcing a ribbon of molten glass under pressure through the slit, and the sheet remains uniformly of the same size in section as the aperture through which it is drawn. Two water-cooled tubes against the sides of the slit serve to chill the glass as it emerges. The original apparatus is shown in Fig. 214. The melting of the glass takes place in a tank, *A*. The extension, *E*, from which the glass is drawn is only separated from the melting tank by the curtain, *B*, so that the molten glass can pass freely from melting to drawing end except at the surface of the metal. Screen *B* serves to entirely separate the two chambers above the glass, and allows the temperature of each to be accurately regulated. Across

the centre of **E** stretch two other curtains, **D**, between which lies the drawing float, **T**. At the works at Dampremy the machines are placed so that a number are served by the same tank, which has an enlarged working end. Above the troughs are placed the drawing machines, rectangular sheet-iron towers four metres high, through which passes a framework with a series of asbestos rollers set in pairs. The rotation of these rollers serves to draw up the sheet as it is formed, and the first pair is situated at about one metre from the surface of the glass. Each roller upon the right is given the same rate of movement by means of a vertical shaft and two bevelled gear-wheels. The rollers on the left are carried on bell-crank levers with counterpoises in order to press them upon the glass, and they engage with the gears of the opposite rollers by long-toothed pinions, which allow for variations when glasses of varying thickness have to be prepared. Inclined sheets **S**, the upper edges of which are on a level with the rollers, serve to prevent radiation of heat and also to receive the pieces of broken material falling when the glass above is cut. The gearing is driven electrically, giving a rate of movement varying from 4 to 40 metres per hour, a rheostat serving to regulate the rate to within 25 cm. per hour. It is found convenient to keep the temperature of the drawing chamber or well at 500° to 600° C. To start the machine, the direction of rotation of the rollers is reversed and a sheet of poor glass passed downwards through them to the float. The latter is then pressed down to give a flow of the desired rate, and the wheels are driven in the normal direction. The glass bait introduced picks up the molten metal and draws it up through the rollers, which are caused to rotate at the speed at which the glass emerges from the slit below.

The rate of working is 30 metres per hour for glass two millimetres thick, with a corresponding diminution of speed with increase of thickness of the glass drawn, so that sheets ten millimetres thick are usually drawn only at the rate of 5 to 6 metres per hour. One machine can produce 23,000 square metres of glass of 2 millimetre thickness per month.

Sheets of glass made by this method are 1 to 1.25 metres wide and are claimed to be uniform in thickness and to be brilliant with a fire-polished surface. The slow, even cooling with no contact with chilling materials gives a glass free from strain which can be cut without trouble by a diamond or cutting wheel. One fault is, however, inherent in the method—the sheets produced contain a number of faint horizontal striæ.

(345) **Colburn's Process.**—I. W. Colburn first commenced his researches in 1900, and in a few years had patented a machine capable of drawing sheet glass, without, however, achieving commercial success. Some years later his patent rights were acquired by Messrs. Libbey and Owens, who, with Colburn's assistance, perfected the machine at their works in Toledo. In 1915 was formed at Charleston (West Virginia) the Libbey-Owens Sheet Glass Company, and a factory was built with a capacity of 600,000 cases of 50 feet each per annum. In 1919 the output was 1,000,000 cases, and the original plant of six tanks was doubled. During 1923 this method produced 25 per cent. of the sheet glass of the

United States. Factories have also been erected in Canada and Japan, whilst others are in course of construction or contemplated in Belgium and other countries.

By the Colburn process, not only single and double strength glass may be drawn, but even sheets 0.25 of an inch in thickness, the latter capable of competing with plate glass for many purposes.

In principle the method consists in drawing a flat sheet of glass by means of a bait, as in the Fourcault system, but the two processes show several vital differences. Instead of using a float to prevent narrowing of the sheet, Colburn in his early machines used two spheres of refractory material carried at the end of long arms and rotating rapidly in opposite directions. The position and direction of motion of the spheres was so arranged that they served to drag outwards the liquid glass as it emerged from the bath, so producing a sheet of uniform width (Fig. 215). The spheres were later replaced by hook-shaped tools, the tips of which moved in an elliptical path in the glass at the point where the edge of the sheet was formed. In the modern machine these methods are discarded and substituted by the use of a pair of water-cooled, channelled

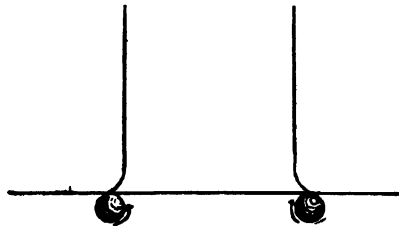


FIG. 215.—THE COLBURN PROCESS.

rollers placed at each edge of the sheet just above the level of the molten glass in the pot. These rollers grip the edges of the sheet as it is drawn and so maintain the width.

Again, when the sheet has ascended vertically to a height of 45 inches, it is softened by gas jets and turned over rollers until it lies horizontally, after which it passes out through an annealing lehr. The method of action of the machine is best explained by reference to Fig. 216.

The melting tank, **1**, is continued by a cooling-off tank, **2**, at the end of which is a smaller forehearth or drawing tank, **3**. A brick curtain **15**, preferably cooled by a water channel, and terminating just above the level of the glass, provides a cooling-off passage for the glass, whilst the temperature in chamber **2** can be regulated by the damper **8** and the opening **9**. The glass is thus cooled to the desired temperature as it passes into the forehearth.

The forehearth itself is supported on pillars, and these form part of a heating chamber in which the burning gases are conducted through passages to the exit flue, **17**. This exit flue is also placed in communication with the space over the drawing tank, which is heated by burners, **20**, curtained by tiles, **19** and **21**. The surface of the glass where the sheet is drawn is protected by two water-cooled screens, **22**. Chamber **30** contains two endless belts, **50** and **60**, for drawing the glass. The belts

are propelled by wheels, the upper belt being provided with caterpillar feet to engage the glass surface and provide a tractive force. To prevent deformation of the sheet as it passes between the belts a plane slipway, **54**, supports the lower belt. A curtain wall, **35**, in the drawing chamber, serves to partly close it, and so form a reheating chamber, **37**, the floor of which is composed of brick, **39**, and block, **40**. Heat is furnished by burner, **41** contained in chamber, **43**, separated from the reheating chamber by a perforated partition. Below **43** is a second heating chamber with a perforated wall, **46**, and a base formed by the projecting fireclay slab, **47**. By suitably regulating the heat from these reheating chambers the slab can be caused to soften sufficiently to bend it at right angles. Two hollow rollers of equal diameter, **65** and **66**, and a smaller roller, **67**, serve to support the glass in bending; they are cooled by air or water. Below the bending roller is a hollow cooling chamber, **68**, provided with

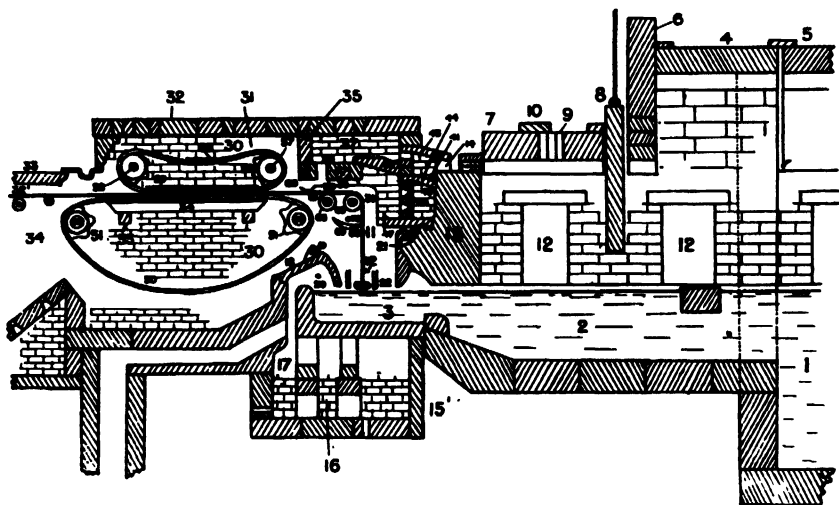


FIG. 216.—THE LIBBEY-OWENS (COLBURN) SHEET DRAWING PROCESS.

water-circulating pipes, **69**, whilst above this is an air pipe, **70**, with jets to cool the portion of the roller, **65**, just about to come in contact with the glass.

Beyond the drawing chamber, **30**, and in line with it, is the annealing chamber, **34**.

To commence operations a glass "blank" is placed on the table, the machinery is started in a "reverse" direction, and the glass so fed over the bending rollers into the metal at the drawing-point. This provides the required bait, since molten glass adheres to it. The belts are run in the normal direction, and a continuous sheet of glass is drawn off, being then cut off in suitable lengths as it emerges from the lehr.

A pair of water-cooled, channelled rollers, **12**, is placed at each edge of the sheet near to where it is drawn, serving not only to maintain the

width of the sheet but also to exert a pull upon the edge (if their speed is regulated so as to be less than that of the drawing table), offering an elastic resistance to the pull of the table. It has been found that the additional tension placed only on the edge of the glass, but not in its centre, by this means serves to remove unevenness and prevents deterioration of the sheet. The best results are obtained when the peripheral speed of the grooved rollers is 10 to 20 per cent. less than that of the drawing table. The rollers are separated by a distance rather greater than the thickness of the sheet of glass, which latter consequently possesses somewhat thickened edges.

It is necessary to emphasise that the bending roller, 65, must be cool as it comes into contact with the glass, or else deterioration will ensue. The marking of the glass by this bending roll constitutes one of the difficulties of the method, and various plans have been tried to remedy it. In one, the soft glass, before passing through the tractors, is smoothed by special smoothing irons. In another, the roller is made of wood, is cooled just before contact by dipping in water, and revolves at a slightly different rate from the glass passing over it. In a recent variation two sheets are drawn from the same forehearth and pass together over the rollers, then through the belts. The lower sheet passing directly over the bending roll protects the upper, so that whilst the latter is of very good quality, the former is quite saleable. Whether this modification will supersede the original method remains to be seen.

Heating is obtained at the Charleston factory by means of natural gas, but other works are equipped with producers. As originally designed, one machine was attached to each tank, but as a measure of safety a start has been made in providing tanks with two machines. Since the action is continuous, each drawing apparatus is equivalent to forty-four blowers using hand methods and it is capable of producing 10,000,000 square feet of single strength glass per annum. The sheets are about 72 inches in width. They are drawn at the rate of from two to six feet per minute, depending on the thickness of the glass.

Quite recently attempts have been made by the same workers to draw wire glass by a similar method, that is, by running a continuous wire sheet horizontally from a tank of molten metal.

During the past few years a number of other sheet-drawing processes have been patented, many of them similar to the above, but some using the method of causing the glass to flow on to special surfaces. None of these are as yet known to be commercially successful.

(346) **Cylinder Drawing Machines.**—Attempts at drawing sheet glass in the form of long cylinders were made by M. A. Oppermann at Charleroi in 1885. The process first attained importance in 1905, when a commercially successful process was patented by J. H. Lubbers of Pittsburg, Pa., as the result of endeavours commenced in 1894. Details of Lubbers' machine will be found in Fig. 217. The process consisted in dipping a hot "bait" into a drawing-pot containing the molten glass and, when the metal was attached to this bait, withdrawing it at a sufficient rate to form a cylinder of glass of uniform thickness and diameter. To prevent the cylinder wall from falling in as the draw continued, air under pressure was admitted to the interior, the air pressure

being so regulated as to keep the wall vertical. The following details serve to indicate the method by which the cylinder was drawn. The

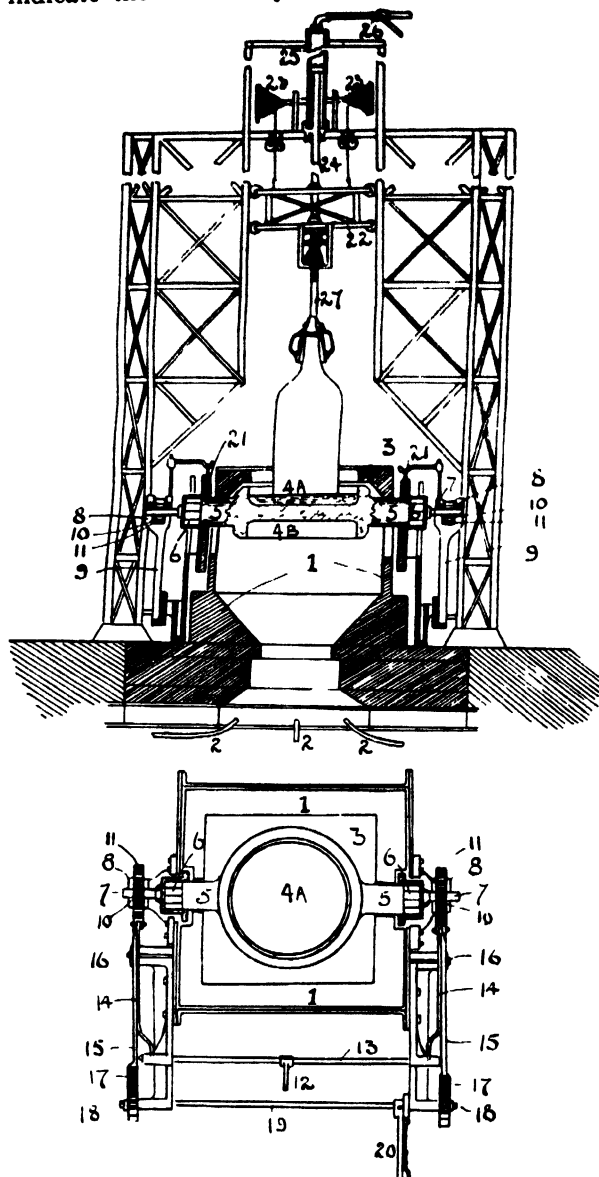


FIG. 217.—THE LUBBERS CYLINDER DRAWING MACHINE.

furnace, 1, was made of sheet iron lined with firebrick, and was built over a pit. Its upper portion was rectangular, with a central cylindrical

opening to receive the pot, but towards the base this tapered conically, whilst lower still were mounted gas burners, **2**, capable of maintaining the interior of the furnace at a fairly high temperature. A large slab, **3**, possessing a circular opening of a diameter equal to that of the interior of the pot served to cover the furnace top after the latter was introduced. The drawing pot consisted of a double vessel; that is, it possessed two cavities, **4A** and **4B**, each of about forty inches diameter, placed base to base. It was prolonged at each side into cylindrical arms, **5**, terminated by polygonal ends, **6**, the whole forming a single mass of refractory material. Fitting the ends of the arms were metal caps which served to attach simple bearing axles, **7**. The axles rested in forked bearings, **8**, placed on vertical supports, **9**. In the recesses of these bearings were attached to the axle, pinions, **10**, which engaged with short horizontally-moving racks, **11**, below. These racks were governed by the single lever, **12**, acting through the cross-shaft, **13**, and the connecting rods, **14**. By movement of this lever, transmitted through the racks, the crucible could be rotated and either of its cavities brought to the top. The supports, **9**, moved in vertical guides and were attached at the bottom to sloping levers, **15**, pivoted at **16**. Segmental racks, **17**, terminated the upper ends of the levers, these engaging in pinions, **18**, mounted on the shaft, **19**, and controlled by lever **20**. The height of the pot in the furnace was thus governed by lever **20**. In order that the vertical movement of the pot might be possible, vertical slits were provided in the furnace sides, and radiation of heat from the slits was prevented by the brick-lined screens, **21**, capable of being raised or lowered with movements of the pot. To shut the furnace top as far as possible, the outer edges of the drawing pot were chamfered and the inside edge of the slab, **3**, bevelled at the same angle, the two surfaces engaging closely, so forming a good joint.

Cylinders were drawn from each cavity of the pot in turn, and when one drawing was complete the pot was lowered in the furnace, rotated through an angle of 180° , then again raised to its original position. The unused glass in the first cavity was melted by the burners below and ran out of the pot into the recess beneath the furnace, whilst the pot itself was heated up for a fresh charge. Sufficient molten metal was at the same time poured into the upper half of the pot to produce a cylinder, the glass being ladled from the melting tank by a large, mechanically-supported iron ladle, capable of transferring a full charge at one delivery.

Surmounting the furnace was an iron framework, of height greater than that of the cylinders to be drawn, having a vertical track in which ran the carriage, **22**, mounted directly over the pot. The carriage was supported by wire ropes mounted upon drums, **23**, electrically driven. To the carriage was attached a long iron tube, **24**, whose upper end moved, piston-like, in a tube, **25**, of wider bore, immovably fixed to a crossbar of the framework. Tube **25** was connected to the compressed-air supply by a tube provided with a cock, **26**. At the bottom end of the movable tube was joined the blowing iron, **27**, about three feet long, similar to those used for hand-working, with the exception that the nose was fairly large, in order to retain heat during the drawing period. Before

the drawing commenced the nose of the pipe was heated in order to secure attachment of the glass to the iron.

Having filled a charge into the drawing pot and allowed it to reach the correct temperature for drawing, the heated bait was lowered into the molten metal, contact was secured, and the tube slowly withdrawn. At first the air was supplied at a low pressure; then the air-pressure and speed of drawing were increased, by which process the diameter of the cylinder was brought to, and maintained at, the required value. During the remainder of the drawing the air was supplied to the interior of the cylinder at constant pressure, but in gradually increasing amounts. The drawing of a cylinder forty feet in length required about fifteen minutes, during which time the glass in the pot was cooling and its viscosity and surface tension increasing. For this reason, to secure a cylinder wall of uniform thickness, the rate of drawing was increased steadily as the process proceeded, a result obtained by using tapering drums, 23, and running them at a constant speed.

When complete, the cylinder was cracked off by so rapidly increasing the rate of drawing that the wall became exceedingly thin, when it could be broken away from the pot with ease.

The lowering of the cylinder was no easy matter, and was most easily performed by pulling aside the bottom by means of a rope and trolley, then lowering the bait until the glass rested upon a rack of semi-circular bearing arms.

At this stage it was cut into lengths of five feet by means of an electrically heated wire, split open and flattened as in the hand method.

Several weaknesses in the foregoing method have in recent years been remedied. The gravest fault was the danger of cracking off of the cylinder from the bait during drawing, due to the too rapid cooling with consequent contraction of the iron.

The pipe has been generally replaced by a bell-shaped iron bait, twelve inches in diameter, with an inwardly projecting rim around its lower edge. A channel is thus provided into which the glass flows and solidifies to give a supporting lip during the drawing operation (the bait is usually electrically heated). In one form of apparatus, a bait made of an iron-nickel alloy having the same coefficient of expansion as glass serves as a preventative to premature cracking off.

(347) **The Frink Cylinder Process.**—In the Frink cylinder machine the pots, two in number (and single in shape), are mounted upon a central vertical shaft, and as they revolve come in turn under the bait. Compressed air is let into the cylinder from below, by means of a fireclay pipe passing through the centre of the pot. A ring bait of a diameter equal to that of the cylinder to be drawn is employed. After the drawing, a horizontal revolution of the pot through an angle of 180° brings it into the reheating furnace, where it is overturned and cleaned out as before.

In the cylinder process it is most essential during the drawing that the bait should remain accurately centred over the pot, since otherwise glass is not drawn from an isothermal zone and a wall of irregular thickness is obtained. Large cylinders may attain as much as 1,000 lb. in weight, and the metal is supplied from large tanks each capable of supplying 8 to 12 cylinder machines and holding 2,000 tons of molten glass,

with a daily melting capacity of 400 tons (the size of the tanks is 140 by 38 feet with a depth of metal of 5 feet).

It must be emphasised that the cylinder method involves large wastage of glass, both that which is chilled at the edges of the ladle (and consequently must not be poured into the pot) and the residual glass in the pot after drawing. This glass can again find employment as cullet.

A number of recent patents are based on the use of forehearth in tank furnaces as drawing pots. The pots are so devised that molten glass flows into the pot as desired, and the use of ladles for carrying the glass, and also the need of reversing the pot for emptying and reheating, is avoided.

CHAPTER XXXV

THE MANIPULATION OF GLASS—*Continued*

V. Plate or Rolled Glass.

(348) **Types of Plate Glass.**—One other method of forming window and mirror glass remains to be described—that is, the production of “cast-plate” glass. Plate glass is generally manufactured by pouring the molten glass on to a large iron casting table and rolling it to a definite thickness by means of a heavy iron roller, usually mechanically driven. The thickness of the plate is regulated by the use of two iron slips laid along the edges of the table, on which the roller rests. Thus, by using slips of different depths, glass plates of varying thickness are obtained. To adjust the width of the plate and to prevent glass from flowing on to the side slips, two guides of cast-iron are rested upon the table at the required distance apart. These guides are shaped to fit the front of the roller and are driven forward by it, so governing the width to which the glass spreads during the rolling process.

Three types of plate glass may be distinguished: (1) Rolled plate (or rough-rolled), in which the glass surface is left untreated after rolling and annealing, and is consequently rough; (2) polished plate, in which the first type, after annealing, goes through a process of grinding and polishing; (3) figured rolled plate, where a pattern is impressed upon one side of the glass during the process of rolling. We will describe the production of each of these in turn, and supplement the description by some allusion to glasses of similar nature—namely, wire glass and heat-resisting structural glass.

(349) **Rolled Plate.**—This is the cheapest form of glass used for glazing, being employed for skylights, etc., where transparency is not a vital factor and only translucency is to be considered. The glass is rough and common in appearance; it is usually made in the simplest manner with cheap materials. A usual batch is one of the sand-limestone-salt-cake type, fairly low in alkali, the most expensive of the substances employed. Melting is performed in continuous tank furnaces, simple in type and capable of a large output, in some cases up to 150 tons per week. Irregularities in the finished product tend to hide minor defects, such as small stones or seed, so that great care in melting and fining is not necessary. In fact, quantity and not quality is the governing factor in the production of this type of glass. The composition of the glass made, however—*i.e.*, its low alkali content—calls for a fairly high melting temperature.

In the process of casting, molten glass is gathered from the tank and transferred to the table by means of large iron ladles capable of holding

in some cases up to 200 lb. of glass. After the glass is gathered, the ladle is supported by an overhead pulley and balanced at the end of the handle by the gatherer, who then transfers it to the table and pours it just in front of the roller.

The metal chilled by contact with the iron must be retained in the ladle and returned to the tank, or so poured that it lies at the edge of the metal on the table and after rolling can be easily detached and removed.

When rolling is complete the glass is allowed to remain until sufficiently set; it is then loosened from the table by a rapid movement of a flat iron blade, transferred to a flat stone, and from thence to the annealing lehr. This lehr is of similar design to that used for sheet glass, and the plate is moved along by a series of grid bars. From the end of the lehr the annealed sheets pass to the cutting room, where they are trimmed by means of a diamond to even shape and desired size, whilst the obviously faulty portions are noted and removed.

(350) **Polished Plate.**—Of recent years there has been a tendency, due to increased demands, towards the production of larger and yet larger sheets of polished plate glass. Whilst in 1844 the limiting size was about 130 square feet, tables are now in common use capable of rolling sheets of a surface area of 400 square feet and weighing up to 3,000 lb. This increase of size, coupled with the large output, has necessitated the introduction of mechanical means of working, with labour-saving devices, generally electrically controlled. For instance, in some of the more modern works most of the process of casting and rolling is under the guidance of one man, who works as many as seven controls performing nine distinct operations.

Glass for polished plate is melted in open pots of a size conditioned by the size of the casting table, but of an average capacity of 2,000 lb., which is sufficient for a table 24 by 14 feet, giving a plate 300 square feet in area. Rectangular regenerative furnaces are the type usually employed, and these contain 16 to 20 pots arranged in two rows on opposite sides of the furnace. The front of the furnace, before each pot, is closed by a gate, counterpoised so that it can be readily raised when the pot is removed. It is customary to actually remove the pot from the furnace and pour the molten metal from it directly on to the casting table. Since this process subjects the pots to heavy strain they must be well built and carefully annealed before use. This involves a very careful and slow preheating in the pot-arch, during which time the temperature is raised gradually to 670° C. It is then placed into the furnace and its temperature allowed to reach about 1440° C., when the batch is fed in. Batches of the usual mixed soda-ash, salt-cake type are most favoured, a common batch formula being sand 1,000 parts, limestone 320, soda-ash 310, salt-cake 65, charcoal 3, giving a glass of a composition SiO_2 72 per cent., CaO 13 per cent., Na_2O 15 per cent. From the nature and employment of the finished product, materials of good quality are essential, points discussed elsewhere in this volume, whilst melting and fining must be complete. In fact, the glass required for polished plate, since the cost of production is so heavy, and the faults so liable to lead to disaster in subsequent operations, or so obvious in the glass when completed, must be as free from stone and seed as possible.

It must be nearly colourless, although plate glass has generally an appreciable iron oxide content, so that, when viewed endways, it shows a distinctly green colouration.

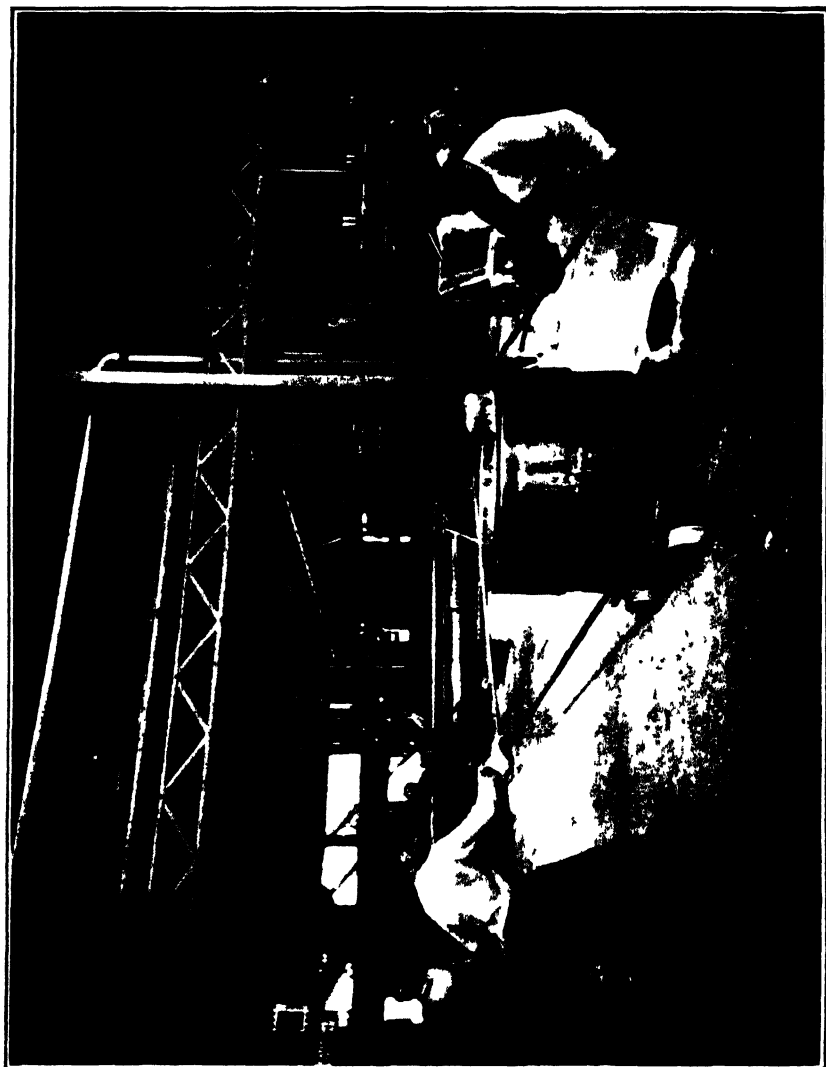


FIG. 218.—SKIMMING A POT OF GLASS BEFORE REACHING THE CASTING TABLE.
(Reproduction of the Allentown Plate Glass Co. Glassmen Down Low H. Pendley For "The Glass

For filling in the batch large iron ladles manipulated by hand are employed, although in some works charging is accomplished from a travelling batch-conveyer car equipped with an electrically controlled arm, which is projected into the furnace through a suitable opening. The pot is charged with three fillings, in order to fill it as far as possible,

and melting and fining takes about 20 hours. At this point the furnace is cooled to the casting temperature—*i.e.*, about 1000° C. When the glass is ready for casting the pot is removed from the furnace by means of a goose-neck crane, conveyed to the casting room and there deposited upon a small cable truck. Here it is skimmed to remove impurities (Fig. 218). To pour out the glass on to the casting table, the pot is seized by a clamp suspended from a motor-driven travelling crane (*see* Fig. 219), and is taken to its position over the table. In order that the glass may be uniformly spread over the width of the table it is necessary to move the pot in a direction parallel to the roller as the glass is tipped out.

As we have indicated, modern casting tables are large in size, tables 24 by 14 feet in size and 8 inches thick being usual, whilst some 30 by 17 feet are occasionally employed. The casting plates of such tables are of great weight and may reach as much as 70 tons. It is essential in the formation of plates of glass for grinding and polishing to produce as flat and even surfaces as possible, in order to minimise the amount of material necessary to be ground away, and so, the more the surface of the grinding table deviates from a perfect plane, the greater will be the subsequent labour expended on the sheet. Since it is estimated that a third of the glass is usually ground away, it will be seen how essential it is to keep this to as low a value as possible. For this reason the casting table must be carefully ground flat before use, and maintained as far as possible in that condition whilst the casting process is being carried out. This latter presents some difficulty, since the hot masses of glass heat up the iron considerably but not at all evenly, the centre receiving most of the heat, hence conditions tending towards buckling are produced. To obviate the difficulty, as far as possible, the casting plate is made not in one single piece, but in the form of ten or twelve cast steel bars, each of the length of the table (and of about seven tons weight) closely bolted together, side by side, with cross-bolts in such a manner that expansion of the bars lengthways is not prevented. Even this is only a partial remedy, and the further precaution is taken in practice to perform not more than about eight successive rollings on the same table. L. Rembaux of Belgium has devised a water-cooled table, a difficult matter since the heating is uneven. His method consists in using hollow bars, clamped together, each having a longitudinal dividing wall through the central opening, forming two parallel pipes or channels. Four streams of water run through the plate, beginning at the centre and running by zig-zag paths towards the edges. In the past few years air cooling of the plate has been attempted.

A diagrammatic drawing of one type of casting table, that made by the Benrath Company, is shown in Fig. 220. The table, **1**, is mounted upon a rail track running parallel to a series of annealing ovens, and it is placed with its length transversely to the track, so that it is end-on to the mouth of the oven. Between the table and the oven is another rail track on which is mounted a waggon, **2**, containing the machinery for moving the cylinder and also for driving the casting apparatus along the track. A motor, **3**, serves for the purpose of locomotion, in order to bring the whole opposite to the oven opening, **4**. The roller, **5**, is

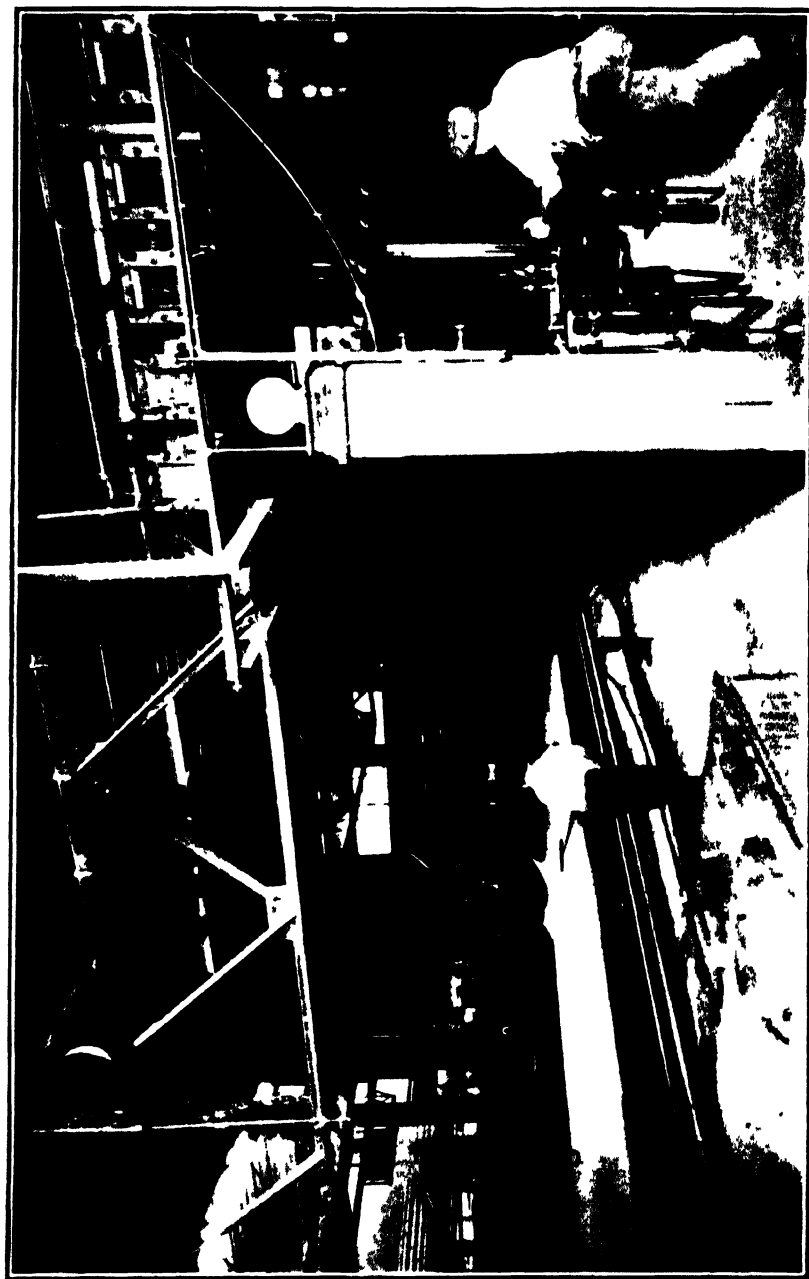


FIG 219.—POURING GLASS ON TO THE CASTING TABLE

(By courtesy of the Allegheny Plate Glass Co., Glassmere, Penn., per H. Proctor, Esq., "The Glass Industry," New York)

about 30 inches in diameter, and is supplied with a slight ribbing, the better to grip the glass. During the time that the glass is being poured upon the table the roller is situated at the end remote from the oven, and is moved over the glass by means of wire ropes passing over pulley 6

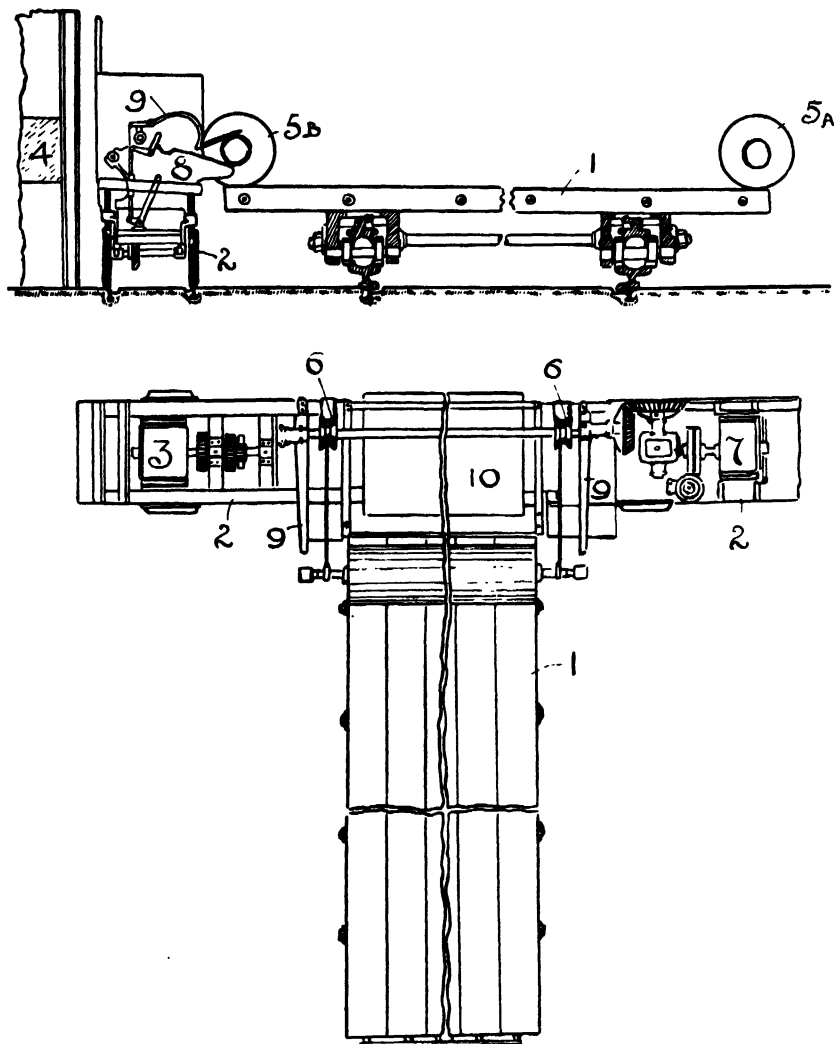


FIG. 220.—A CASTING TABLE MADE BY THE BENRATH COMPANY.

and driven by a second motor, 7. The journey of the roller over the molten glass occupies about a minute. Having arrived at the end of the table towards the oven the roller now ascends the slight incline formed by the upper surface of arms 8, where it is clutched and held by the

arms 9, whilst at the same instant the roller strikes a lever and stops the motor. For transferring the rolled plate to the oven, hooks are provided which are attached to the same ropes used for drawing the roller. When the first rolled end, remote from the oven, is sufficiently chilled, these hooks are attached to it and the plate is drawn into the oven, passing over a supporting plate, 10, on the drawing car. At the end of the operation the hooks strike a lever and the motor is again stopped.

This process of moving the plate presents great difficulties, since the glass must not be allowed to cool too much before being transferred, and yet the end to which the hooks are attached must be sufficiently chilled to resist distortion. Its temperature on leaving the table is about 900°C . By the means just indicated, plates of a size 26 by 14 feet and a thickness of 0.375 to 1.5 inches (or more in special cases) are ordinarily cast.

The table illustrated in Fig. 219 is in use with a modern annealing lehr, and so remains fixed in position adjacent to the mouth of the lehr. For this reason the mechanism for operating the handling of the pot and the moving of the roller and the finished plate can be concentrated at one point, away from the table itself, as shown to the right of the illustration.

Where thin plates of glass are required, say of a thickness less than 0.25 inch, special methods are used, since the grinding down of thicker plates would entail an inordinate amount of labour. At one factory the thin sheets are obtained by using large pots and casting sheets of an area of 450 to 600 square feet with a thickness of 0.28 inch (7 mm.) in the usual way, but employing larger casting tables and much heavier rollers. Immediately the sheet is rolled it is cut up into pieces of suitable size and taken to the annealing oven. Grinding and polishing are performed as for ordinary sheets. A second works uses smaller pots, casts sheets of the same thickness but of smaller size (*i.e.*, 40 to 100 square feet), and performs two meltings daily in each pot.

(351) **The Annealing of Plate Glass.**—Up to the year 1900 plate glass was always cooled in special kilns, but recent years have witnessed the introduction of lehrs for annealing. Movement along the lehr is obtained by means of rods, as described in the chapter on sheet glass, with the difference that the lehrs for plate glass are mechanically worked. Since the sheet is too soft, when first introduced, to be so lifted, it is pushed mechanically through five preliminary compartments, arranged for ease of manipulation so as to give a zig-zag course, after which it passes down the lehr in the ordinary way. The rod lehr for plate glass has a length of about 280 feet.

After annealing, the plates are placed on cutting tables capable of being tilted for ease of handling, and cut into suitable sizes, overhead travelling cranes then conveying the pieces into the grinding room.

(352) **The Grinding and Polishing of Plate Glass.**—It is the process of grinding and of polishing plate glass which has made the greatest strides in recent years, the time required having been shortened to a large extent through the many improvements introduced.

THE OLD OR ORIGINAL PROCESS.—In the old methods three distinct processes were carried out, named respectively grinding, smoothing, and

polishing. The first two were identical in character, and consisted in rubbing down the surface of the glass with flat plates or sheets of iron, using sand as an abrasive. In grinding, the main part of the excess glass was removed by the use of coarse sand, whilst finer sand grains employed in the smoothing process served to eliminate somewhat the large pits and protuberances left by the coarser particles preceding them. After grinding and smoothing, the glass surface had a dull grey appearance. Polishing consisted in rubbing tools shod with felt over the surface of the glass, rouge being used as a polishing agent.

Whilst the first two operations removed large amounts of glass from the plate, the last actually took away no material, but served to level the undulations by a process of flowing or squeezing out, thus eliminating hills and hollows, and producing the smooth surface characteristic of plate glass.

GRINDING.—Up to 1768 all grinding was performed by hand, but about this date machine methods were introduced into England and in time became universal.

The old grinding tables were large sheets of flat stone, upon which the plates of glass were fixed by plaster. A large iron beam, suspended from the roof of the building by chains and swung with a circular motion, served to drag from one to three oak blocks shod with iron plates over the surface of the glass. The workman in charge supplied first coarse, and then successively finer and finer sand upon the table, whilst a current of water carried the sand against the grinding tools. When the first surface was sufficiently ground, the plate was reversed and the process repeated. At a later period the fixed stone table was replaced by a large oak table moving linearly with a reciprocating motion. Two large iron or wood blocks, to which were attached cast-iron plates, mounted on a frame over the table, received a circular translational movement. This double movement, rectilinear of the table and rotational of the grinding blocks, secured a much more rapid rate of grinding, but even so the results were by no means perfect, and breakages reached four to six per cent.

In 1824 Hoyau of Belgium devised a method of grinding, the principle of which lay in the rapid rotation of a number of grinding rubbers, specially mounted, over a large circular table which was designed to rotate about a central vertical spindle. The centres of rotation of the grinding blocks were so placed that all points of the sheet in turn were presented to the grinding action. Hoyau's method was successfully applied in Belgium and slowly but surely supplanted all others, machines of this type being introduced into America, for instance, in 1890.

SMOOTHING.—The first machine for smoothing was designed in England in 1849 by O. Blake, but it was in Belgium that the mechanical process first gained ground. As early as the year 1868 plates of glass were smoothed upon revolving tables at Floreffe, but only in the case of large sheets of glass, smaller ones being still treated by hand or on other types of smoothing table, and it was not until 1883 that the process was applied successfully to all sizes of glass plates.

POLISHING.—The final process of polishing has long been performed by machinery, at first on tables moving reciprocally, and later on

revolving tables—a process introduced in Belgium in 1807. In 1883 apparatus of the type designed by Hoyau for grinding was first used for polishing.

(353) **The Modern Process of Grinding and Polishing.**—At the present time all three processes are performed upon one table, grinding and smoothing in succession by the same tools, using successively finer and finer grades of sand with water until the process is complete. When this stage is finished, the table is removed to the polishing room and the final process of polishing applied. Not only is the time of working thereby shortened, but the glass has to be fastened down to the table only twice, that is, once for each face, as against the six times needed when three distinct processes were employed.

The apparatus consists usually of a circular cast-iron table about twenty-six feet in diameter, mounted upon wheels and set upon rails running from the grinding to the polishing machines. Upon this table are mounted the sheets of glass in a suitable cement—intervening spaces being filled with smaller plates to give an even upper surface and prevent breakage. The table is now run into the grinding machine, where it is caught and held by a circular frame capable of rotating in a horizontal plane. Over the table are two grinding rubbers, large circular discs shod with many small iron blocks, set so as to sweep the whole of the table surface during the rotation of the latter. The runner bars are rigidly held in position, but are capable of being gradually lowered on to the surface of the glass as grinding proceeds. By this means the prominent hilly portions are rubbed off the glass before full grinding pressure is exerted, whilst the rigid nature of the instrument allows of an even surface being more readily obtained than was possible with the older machines. A further advantage is that the machine may be very quickly rotated at full speed, whereas formerly the speed could only gradually be increased. It is essential during grinding that the relative rate at which the glass is removed should be the same over all parts of the table, and for this reason the movement of the glass and of the grinding bars must be carefully regulated.

For grinding purposes the sand is fed on to the table at first in coarse grades, but as the process proceeds in finer and finer grains. The grinding of a square foot of glass employs about 10 lb. of sand, and recently automatic devices have been introduced which, during the operation, receive the sand from the table, classify it into grades, and return the required grade at once to the table. By this means the time of grinding has been cut down to 90 minutes, half the former period.

When the surface of the glass has been sufficiently ground the table is freed from the frame and run to the polishing machine, somewhat similar to the grinding machine, where it is held once more by a frame, and again rotated. The polishing apparatus consists of four revolving frames (see Fig. 221), to each of which is pivoted a number of mechanical discs or rubbers, which freely rotate under the combined influence of the movement of the table below and of the supporting frames above. Thus every portion of the table receives treatment when, by the addition of rouge and water, polishing takes place. The process of polishing takes about 75 minutes, at the end of which period each plate is

reversed on the table and the remaining side is ground and polished as before.

(354) **Examination for Faults.**—At the completion of the polishing process the sheets are washed with dilute hydrochloric acid and polished



FIG. 221 — POLISHING APPARATUS FOR PLATE GLASS
(By courtesy of the Allegheny Plate Glass Co., Glassmere, Penn., per H. Proctor, Esq.,
"The Glass Industry," New York)

lightly with rouge. Careful inspection, performed in a dark room in the case of better quality glass, serves to show faults, which are there-upon marked and as far as possible removed. Insufficiently polished portions are noted, and the plates containing these passed on for further

treatment, either by hand or by small machines, of which many types are in use.

(355) **Bevelling.**—In order to bevel off edges of plate glass when it is needed for mirrors, show-cases, etc., special machines are employed, the most recent now being equipped with emery or carborundum wheels for this purpose. In the Johannet machine, for example, the plate is rigidly gripped upon a bench where it may be adjusted to the one-hundredth of a millimetre by micrometer screws, and is then caused to move slowly against a rapidly rotating grinding wheel, capable of grinding 400 feet of bevelling in ten hours. Since this grinding process produces much heat and so endangers the glass, one machine has been designed to perform the operation under water.

(356) **Silvering.**—Mirror glasses were first covered by silver deposits by Drayton in 1843. The coating is obtained in the following way. After a preliminary cleaning of the glass surface by means of precipitated chalk and alcohol, the sheet is laid in a flat bath with the side to be silvered uppermost. A solution of silver nitrate in water to which ammonia has been added until the first formed precipitate just re-dissolves, is now mixed with a solution of a suitable reducing agent, such as Rochelle salt, grape sugar, or aldehyde, and the mixed solutions at a suitable temperature poured into the bath. The reducing agent throws out of the solution metallic silver, which settles as a close homogeneous layer upon the plate. After a sufficiently thick coating has been obtained the silver layer is backed. Liebig has stated that for a perfect mirror a small amount of a copper compound is also necessary in addition to the silver nitrate.

(357) **Figured Rolled Plate.**—Casting tables used for figured plate are smaller than those employed for polished plate. This is an obvious necessity, since the pattern which it is designed to impress upon the glass has to be engraved upon the base plate of the table itself—a costly process. Such machines possess a casting plate of not more than 12 by 4 feet, whilst for the same reason designs are restricted in number and are of a few common types. It is usual to make the slips upon which the roller runs removable, in order to allow of the finished plate being slid sideways from the table into the lehr. In order to prevent the base plate from buckling with the heat during the casting process it may be provided with vertical ribs on its under-surface, which dip into a trough of water.

To obtain a clearly impressed pattern a fairly soft glass is necessary, and, for effect, this is made brilliantly colourless or is suitably coloured. It will be noted that the upper surface of the glass over which the roller moves is plane, and this is necessary in cutting up the sheets, since it is extremely difficult to mark and break evenly sheets which are figured on both sides.

Recently a machine less costly in character has been designed by Messrs. Chance of Birmingham for preparing figured rolled plate. Two smooth rollers, 1 and 2 (Fig. 222), capable of adjustment, are attached to a fixed iron frame, 3. A plate, 3, is so placed that molten glass can be fed on to it, and so pass between the rollers. Emerging through these, the glass sheet passes along a second short plate and between a second

pair of smaller rollers, 4 and 5, of which 5 is engraved. A further short inclined platform now carries the still soft glass on to the horizontally moving table, 6, whence it is drawn away at the rate at which it is pressed. Cylinders 1 and 2 are of necessity water-cooled, since they come into contact with the hot glass.

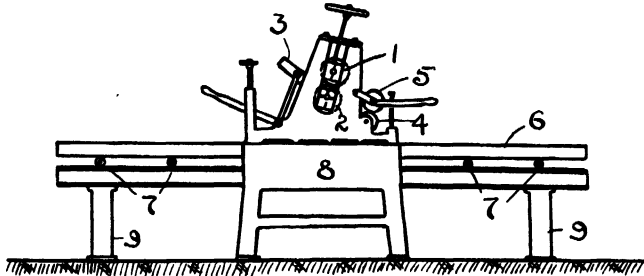


FIG. 222.—A MACHINE FOR FIGURED ROLLED PLATE.

Messrs. Pilkington, of St. Helens, have patented a machine for rolling figured plate glass, both surfaces of which are smooth. In this machine a roller presses out a thin plate of glass on a table in the usual way. Above the table are two other rollers through which a second thin sheet is rolled. The lower of these rollers is engraved to a suitable pattern,

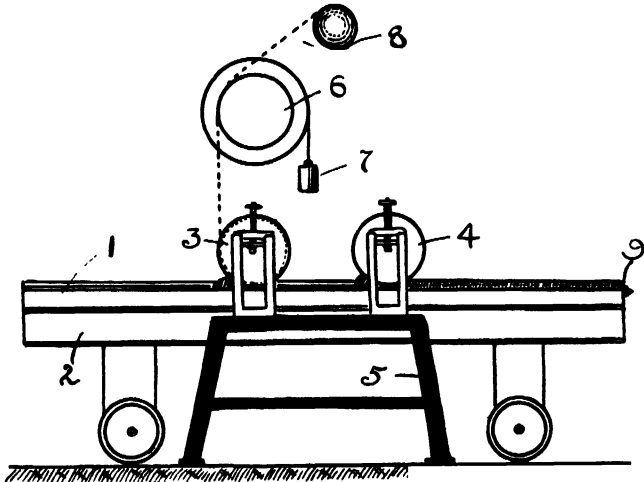


FIG. 223.—APPERT'S MACHINE FOR MAKING WIRE GLASS.

and the sheet so engraved passes down a sloping platform and then lies upon the first rolled plate on the rolling table. A fourth roller now passes over the two plates, still sufficiently soft for it to cause them to unite, and so a plate of glass is obtained with smooth sides, but having a pattern lying along the central zone.

(358) **Wire Glass.**—As compared with polished plate, wire glass is made only in small quantities, but it is now being employed more extensively each year for constructional work.

The glass itself, as in the case of rough-cast plate, is melted in continuous tanks and transferred to the casting table in iron ladles.

Two methods of rolling are employed: (1) The "sandwich" process, in which a thin sheet of glass is rolled, the wire laid over its surface, and a second sheet of glass rolled over the top again; (2) the "solid" process, in which the plate is rolled at once to its true thickness and the wire then forced in by rolling.

(359) **The "Sandwich" Method.**—One of the earliest successful machines was that due to Tenner. A later machine designed by Appert is illustrated in Fig. 223. The rolling plate, **1**, is mounted on a waggon, **2**, running on rails and passing beneath two rollers, **3** and **4**, upon the fixed frame, **5**. Above roller **3** is a cylinder, **6**, having a roughened surface tapering somewhat from centre to sides, and provided with a brake arrangement, **7**. Above this cylinder again and a little to the side of it is the roller, **8**, for holding the wire net.

Before rolling is commenced, wire is run over cylinder **6** and beneath rollers, then finally clamped to the end of the table at **9**, at a height above the casting plate equal to that at which it is desired to embed it in the glass. Glass is now poured on to the table, which is now beneath the roller, **3**, so rolling the bottom part of the plate, the wire being held to the surface of the glass by the pressure of roller **3** and the braking action of cylinder **6**. At the correct moment a further charge of molten glass is poured upon the already rolled plate, in front of the second roller, **4**, and this now completes the plate by rolling out a glass layer above the wire. Since the first layer of glass is still soft, the two layers unite to form a single plate.

(360) **The "Solid" Process.**—A machine introduced in America by F. Shumann in 1892 has proved very successful in the manufacture of wire glass by the solid method. Its operation requires three rollers, **1**, **2**, and **3** (Fig. 224), mounted upon a stand so as to move together over the casting table. Rollers **1** and **3** are smooth, but the middle roller, **2**, has a number of ring-like projections, **5**, upon its surface. Wire is supplied along a slide, **6**, between rollers **1** and **2**. To operate, glass is poured on the table and rolled out to the thickness of the desired plate by roller **1**. Wire is now laid upon the plate by the slide, **6**, travelling in front of roller **2**, the rings of which press it to the desired depth into the glass. The third roller, set at the same height above the table as the first, finally rolls above the now corrugated sheet and once more smooths it out. A modification of the Shumann process by P. Chauvel presses a number of parallel wires into the glass instead of netting, otherwise the method being the same.

Recently a very simple solid method of rolling wire glass has come into operation. In this process wire is clamped above the table at the correct height, and glass is poured on and rolled in the usual way. The roller forces the fluid glass through the meshes of the wire, to unite again beneath it, so giving in one simple operation the required result.

Several important difficulties attend the production of wire glass.

In the first place, differences in the coefficient of thermal expansion of glass and wire tend to cause disruption of the plate when the glass cools, and rolling must be carefully performed to prevent this. Recently an iron-nickel alloy of similar rate of expansion to the glass has found employment in the formation of wire netting. Impurities also on the surface of the wire, and gases contained within the metal, tend to produce bubbles in the glass during rolling and prevent perfect attachment. Wire glass is much stronger mechanically than plate glass, hence its value for constructional work. A sheet of corrugated wire glass 3 by

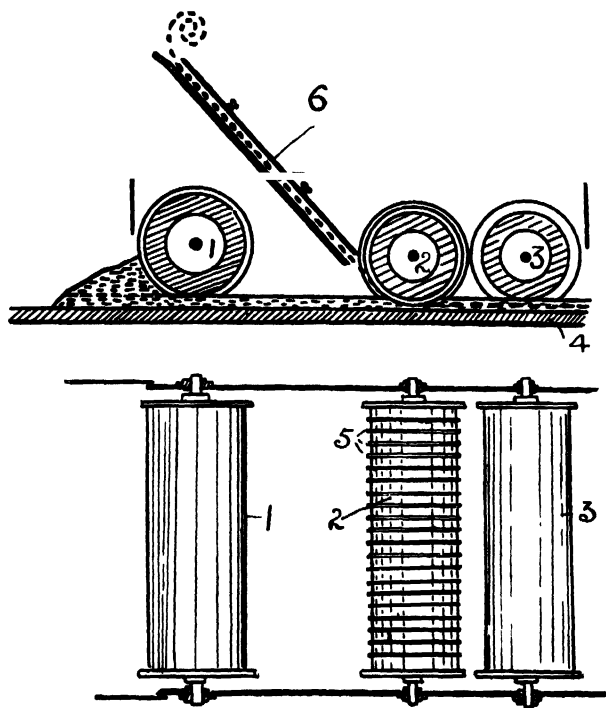


FIG. 224.—SHUMANN'S MACHINE FOR MAKING WIRE GLASS.

6 feet, on knife edges almost 6 feet apart, sustained a load of 400 lb. near its centre, and after heating and cracking with water it supported the weight of a man.

It is quite possible to grind and polish the surfaces of wire glass, and polished wire plate is fairly extensively used, whilst figured rolled wire plate is also manufactured.

(361) **Heat-Intercepting Structural Glass.**—The fact that certain compounds cut off the heat rays passing through glass into which they are incorporated has been long known, but its application to the manufacture of structural glass is of quite recent date. L. T. Sherwood, after many attempts, evolved a glass which, worked up into polished

plate, was capable of absorbing 78 per cent. of the heat rays. His batch consists approximately of sand 1,000 parts, soda-ash 308, borax 15·4, limestone 154, nitre 30·8, manganese dioxide 0·15, titanium oxide 0·05, nickel oxide 0·06, artificial biotite 31.

The artificial biotite is used in place of natural biotite, previously found to increase the absorbent effect, and is made up of micaceous hæmatite 40 parts, precipitated alumina 5, solid sodium silicate 50, magnesite 5, manganese dioxide 0·066, all finely ground and thoroughly mixed before adding to the batch.

This glass is melted in continuous tanks under oxidising conditions, whilst careful manipulation of the flame temperature is necessary to produce a successful glass. The glass is now made in many forms, such as polished plate and wire glass, either rough or corrugated.

Messrs. Chance Bros. and Co., Ltd., of Smethwick, produced, in 1923, a specially tinted rolled glass which cut off over 60 per cent. of the heat of the sun whilst at the same time transmitting over 60 per cent. of the light. The great advantages of such a glass for roof glazing in hot climates are obvious.

CHAPTER XXXVI

THE MANIPULATION OF GLASS—*Continued*

VI. The Manufacture of Rod and Tubing.

(362) **Nature and Uses.**—A large demand for rod and tubing comes from "lamp-workers," makers of chemical and physical apparatus, who, for this purpose, fashion the glass with the aid of the blowpipe flame. We may cite, amongst the many articles made from glass tubing, test tubes, burettes, condensers, certain types of vacuum pumps, etc., whilst the filament carriers in electric lamps absorb a large amount of tubing and of cane. Coloured rod and tubing is used extensively for making fancy articles, such as buttons, bangles and beads, and for the manufacture of glass eyes.

The glass from which tubing is made varies according to the purpose for which it is required. Combustion tubing, for instance, consists of a hard glass of high softening point, and for this purpose a potash-lime glass of high silica content is employed. For lamp-working and general purposes a soft soda-lime glass is preferred.

(363) **Hand Methods of Manufacture**—**ROD.**—The requisite amount of molten glass is gathered on an iron and marvered into the shape of a thick cylinder. On a punty or post with a flattened end is taken a small gathering of glass, which is shaped into a suitable condition for the attachment of the parison, that is, into a flat disc.

The parison is meanwhile reheated at the furnace and, when soft, held vertically so that the end slowly sinks, touches and adheres to the glass on the punty held directly beneath. When attachment is complete the two workmen engaged in the process, one holding the gathering iron, the other the punty, walk rapidly in opposite directions over a wooden track or runway, on which the glass rod, as it is drawn out, gradually comes to rest. The rate at which the men move decides the distance apart which they finally attain, and consequently the thickness of the rod produced. Cane so made needs no annealing, and when cool is cut up into suitable lengths. Uneven portions are rejected, whilst the rest is sorted according to diameter.

TUBING.—The only difference between the mode of making tubing and the above described process for rod is that the glass is gathered on a pipe and first worked into a thick-walled hollow cylinder, which is then drawn out as before.

(364) **The Danner Tube-Drawing Machine.**—Although the Danner machine is simple in principle, it has nevertheless proved very efficient in practice. In this machine (which is patented by the

Libbey-Owens Company) a band of molten glass flows regularly and evenly over a lip, and falls a short distance on to a cylindrical or conical fireclay sleeve held upon an inclined rotating mandrel. The mandrel is set in a plane at right-angles to the direction of flow of the glass, and is surrounded by a muffle maintained at a suitable temperature. By this means a sheath of molten glass forms over the sleeve and slowly flows towards the lower end of the mandrel, which is set against an opening in the wall of the furnace. By the use of a suitable apparatus this sheath of glass is pulled away as it flows from the nose of the mandrel,

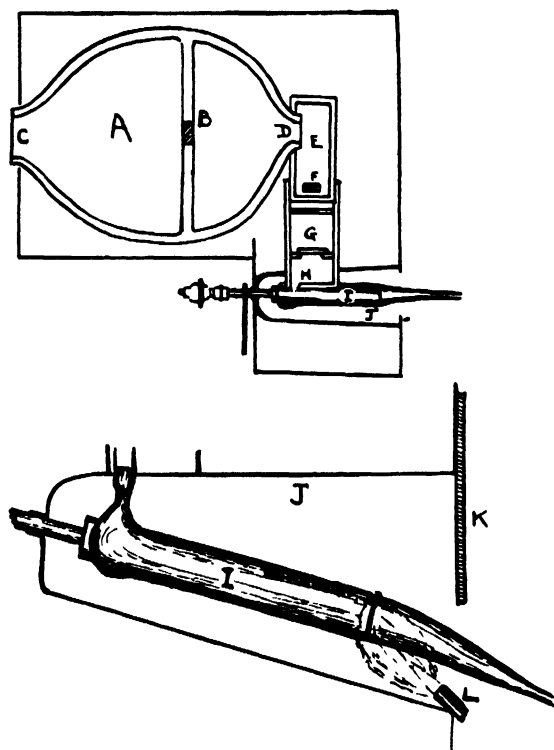


FIG. 225.—THE DANNER TUBE-DRAWING MACHINE.

either as tubing or as rod as may be desired. General details of the process will be grasped by consulting Fig. 225. The glass may be melted either in tanks or pots, the tubing or rod being drawn in a small subsidiary furnace in which the mandrel is situated. The illustration indicates a plant designed for making lead glass tubing which is melted in pot furnaces of the usual type. The subsidiary furnace holds a large pot, A, of a somewhat unusual design. This pot is oval in section and is divided into two compartments by a wall, B, in the bottom of which is a dog-hole connecting the two chambers. Glass is ladled into the

pot at the mouth, **C**, at a rate regulated by the speed of working and the size of tubing in process of manufacture. At the back of the pot is a smaller oblong opening, **D**, through which glass flows in a stream which then falls about three inches into a shallow trough, **E**, so set as to cause the glass to flow in a direction at right-angles to that which it possesses on leaving the pot. It is claimed that, by cascading the glass in transit, the presence of seed is largely eliminated. The bottom of the trough shelves slightly, and in it, near to the end remote from the pot, is an oblong opening, **F**, through which glass passes into a second trough, **G**. This is some ten inches deep, and is divided into three portions, firstly by a wall with a dog-hole at the bottom, secondly by a gate capable of adjustment so as to regulate the rate of flow of glass into the third and final compartment. At the end of this trough is a channel, **H**, two inches broad, set at the corner adjacent to the pot, and through this channel flows regularly and evenly a band of glass two inches broad and half an inch thick, which then falls a distance of four or five inches on to the mandrel, **I**, below. The two troughs are set in an extension of the furnace and can be heated as desired.

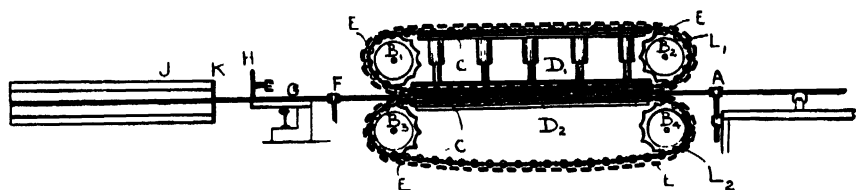


FIG. 226.—THE DANNER TUBE-DRAWING MACHINE.

The mandrel itself is an iron tube, the shoulder of which projects through an opening in the back wall of the muffle, where it is driven by means of a sprocket wheel and chain. A cylindrical fireclay sleeve, turned accurately to size, slips over the mandrel and is secured in position by a nichrome nose. Inside the mandrel is an iron, water-cooled tube with a nozzle through which a jet of air, at, or slightly above, atmospheric pressure, can be blown, and it is this air jet which serves to keep open the bore of the tube. If it is desired to make rod a cap is screwed over the nozzle and the air blow so prevented. Of great importance is the accurate adjustment of temperature of the chamber in which the mandrel is situated (this being about 900° to 950° C.). In one form designed, a rotating metal sheath is used, suitably heated from without. A form found to give good results consists simply of a fireclay muffle, as shown at **J**, heated by burners, and capable of being closed by a gate, **K**. In addition, a gas jet, **L**, plays upon the nichrome nose, keeping this at a suitable temperature. When the machine is first started the glass, as it flows off the mandrel, is seized and carried along a runway to the drawing apparatus, into which the end of the tubing is placed.

The pulling device is set at a considerable distance from the furnace in order to allow the glass to set before tension is applied; thus for tubing three-sixteenths of an inch in diameter it is fixed at a distance of 100 feet from the furnace. Between the furnace and the pulling device the

tubing is supported by a set of grooved wheels arranged upon the running track, and it finally passes between two guiding wheels, **A** (Fig. 226), set on vertical pivots.

The pulling apparatus consists of two endless chains, **L**₁, and **L**₂, above and below the tube respectively, working on sprocket wheels, **B**₁, **B**₂, **B**₃, and **B**₄. The bearings of the upper wheels can be simultaneously adjusted in a vertical direction by a single screw to allow of the regulation of the distance between the upper and lower chains. In each link of the sprocket chains is placed a roller, **C**, and these rollers, during part of the journey, press against the plates, **D**₁ and **D**₂. The lower plate, **D**₂, is fixed, but the upper one is adjustable and divided into independent portions. This allows the pressure between the two chains to be adjusted, in order to allow the tubing to be securely but safely gripped, whilst sliding friction between the plates and the chain is avoided by the use of the rollers. Alternating with the rollers and attached to the same shafts are shaped gripping pads, **E**, which actually serve to hold and pull the tubing along. As the tubing leaves the pulling apparatus it passes between a second pair of guide wheels, **F**, and then above a short table, **G**, the end of which is pressed upwards by a spring. This pressure serves to hold the glass against a cutting wheel, **H**, which descends periodically, whilst at the same time moving laterally at the same rate as the tubing, and nicks the latter. Breaking off is performed by a paddle wheel, **J**, consisting of a central shaft with vanes arranged around it in the form of pockets, and a plate, **K**, covering the end and provided with suitable openings for the admission of the tubing. When a length of tubing, almost up to the cut, has passed into one of the pockets, the shaft rotates just sufficiently to break off the glass and expose the succeeding pocket. The length of tubing severed falls by gravity from the pocket into a suitable holder, from which it is removed as desired.

For tubing three-sixteenths of an inch in diameter the rate of production is about 140 feet per minute. Since each portion of the tubing is identically treated it is perfectly uniform in bore and thickness, a condition not obtained by hand drawing, where the central portion is narrower than that at the ends.

CHAPTER XXXVII

OPTICAL GLASS

The Necessity for Research.—We have already discussed, in the chapter dealing with physical properties of glass, the variation of essential optical properties—namely, refractive index and dispersion, with chemical composition. It will be evident from what was there stated that successful production of optical glass depends essentially on the formation of a clear, homogeneous glass of perfectly definite composition. What that composition must be is decided by the optical constants required. Batches used by firms producing optical glass are, in general, based on the result of long and detailed research, and are not divulged by them. Of late years much work has been published whereby the composition of many optical glasses has been made known, but even now, the successful manufacture of a sufficiently large number of glasses to form a satisfactory optical series can only be undertaken by any firm willing and able to spend much time and money in preliminary investigation. It may also be said at this point that such are the inherent difficulties connected with the process that usually not more than 20 per cent. and often not more than 10 per cent. of the glass made is fit for sale for optical purposes.

(365) **The Conditions Required.**—The following conditions must all be considered in this branch of glass-making, and inattention to any one of them will most likely lead to failure. In the first place, each glass produced must have fixed refractive indices for various wave-lengths of light, and the values for any particular glass must remain, within very narrow limits, the same for successive meltings. The refractive index of the **D** line, for instance, must not vary more than ± 0.001 , and the ν value more than ± 0.1 . But although this is important, it is by no means the only essential of a good optical glass.

Durability must be a prime factor, since it is no use spending time or money on a glass which would become dimmed or undergo disintegration on usage.

Again, the glass must be extremely free from seed and bubble. It may be remarked that this is almost as much a matter of appearance as of optical efficiency. A small bubble in a lens will probably cut out not more than about one six-thousandth part of the light, but manufacturers of optical instruments, in deference to public opinion, will not use such a lens.

Veins or striæ must also be absent, even such fine ones as would be invisible to the naked eye, and so necessitate other means of detection.

Optical glass must be practically free from colour, and this must be secured by absence of impurities, since addition of decolourisers results in diminished transmission of light.

Further, the glass can only be considered satisfactory if it allows itself to be worked into lenses and prisms, and is not prevented by hardness and brittleness from being ground and polished. Another essential also is that the glass, when molten, must not be too viscous to admit of easy stirring.

Even when the glass itself answers all the above requirements, it is not always easy to secure a suitable batch for producing it, since the mixture must be capable of easy founding under normal conditions.

One essential of the process, as we shall see, lies in cooling the glass, when made, sufficiently slowly to obtain large pieces, and this slow cooling tends to facilitate devitrification, to which some types of glass are so prone that they must be excluded from the list of possible optical glasses.

Should all the above difficulties have been overcome, a further trouble awaits the manufacturer, in that annealing of the glass must be so thorough as to free it perfectly from strain, by no means a simple proceeding.

Apart from the difficulties connected with the glass itself, there is the trouble of obtaining pots able to withstand the corrosive action of molten glass sufficiently to avoid serious alteration of the composition of the glass they contain. The provision of good pots is one of the most fundamental necessities of the process, and it is to be hoped that faults in this direction will, before long, be minimised by the discovery of a sufficiently good refractory material.

We will now consider in detail the process of manufacture with particular regard to the essentials noted above.

(366) **The Batch Materials.**—Only the purest substances obtainable can be employed in manufacturing optical glass; not only must they be practically free from iron and iron compounds, but they must be constant in composition, whilst they must be carefully analysed so that a batch giving glass of the desired composition may be obtained.

The substances used are much the same as have been indicated for other kinds of glass, except that some firms prefer potassium bicarbonate in place of the carbonate, since the former can be obtained in an extremely pure condition. In almost all cases 25 to 30 per cent. of the potash in the glass is supplied as nitrate, and in one works, where specially resistant pots are employed, larger amounts still of the carbonate have been replaced by nitrate; sometimes even the whole of it has been so substituted.

The materials are dried and sieved before use, afterwards being accurately weighed out and extremely thoroughly mixed. When weighing of the batch takes place, alterations later to be encountered, such as absorption from the pot of appreciable quantities of silica and alumina, and loss of materials by volatilisation during melting, must be allowed for. These corrections can only be judged by experience. Some manufacturers prefer mixing in the old type of trough by means of wooden shovels, with a final sieving; others, again, use one of the numerous drum types of mixers on the market. All apparatus must be cleaned

before use to prevent contamination, not only by outside impurities, but also of one batch by another. It is best to use, when possible, the whole of the batch immediately after mixing, but if some must be stored, dry, closed bins should be provided. As a rule, individual batches weigh from 10 to 15 cwt., according to the size of the pot used or of the type of the glass to be made. Since much of the glass is rejected for such defects as *striae* and seed, it is evident that, when necessary, much cullet is available.

Difficulty attends its use, since it can only be again employed for glass of exactly the same composition; for this reason no mixing of various kinds of cullet can be allowed. Again, each time the glass is melted, more impurities are picked up, particularly in the case of heavy lead glasses, and further changes are induced by selective volatilisation. All these dangers restrict the employment of cullet, and no rule can be laid down as to the extent of its use, circumstances alone deciding this question.

The cullet must be broken, and for this purpose a jaw crusher, with subsequent magnetic separation of the iron particles introduced, may be employed.

(367) **Furnaces and Pots.**—Because of the careful regulation of conditions required in melting optical glass, single furnaces, approximately cubical in shape, capable of holding one pot only, are almost universally employed. Heating is provided by means of town's gas or producer gas, in the latter case with regeneration of heat.

Some varieties of glass can be melted in large regenerative furnaces holding about twenty pots, and similar to those employed for plate glass manufacture, but this method is by no means common.

As a rule, the pots are about three feet in diameter, with walls 3 to 4 inches thick, and for protection of the glass they are very often of the covered type. Choice of pot clay is vital, and pot-making must be of the best, in order that pot attack shall be reduced to a minimum. We must refer the reader to the section on pot-making to follow how this is obtained. Preheating of the pot in the pot-arch takes several days, during which time the temperature is slowly raised to 1000° C., after which the pot is introduced into the furnace in the usual way. The temperature to which the pot is then subjected is dependent upon the kind of glass to be produced, dense flint, for instance, requiring a temperature not much above 1000° C., whilst boro-silicate and hard crowns may need founding at 1500° C. An average temperature for many types of optical glass is about 1400° C. Once the temperature is reached it must be maintained with great care, since variations of even 30° C. are liable to introduce errors, and to this end all furnaces are equipped with temperature recorders. The pot is first held at the melting temperature for about an hour, to complete baking and to give it as dense a condition as possible, in order to resist the corrosive action of the glass. It is then glazed internally with cullet (a process already described), in order to protect against molten batch materials, and a further hour's standing is given.

(368) **The Melting of the Glass.**—Next comes the filling on of the batch, a process performed in a series of additions in the usual way. With closed pots a layer of metal 18 to 20 inches deep is conveniently

melted; with open pots batch is added until the glass stands about one inch from the rim of the pot. Melting, which now takes place, occupies up to ten hours, and leaves the glass seedy, fining then being obtained by suitably raising the temperature and leaving the glass several hours longer, after which the surface is skimmed to remove any impurities. In England, stirring is not commenced until fining is complete, but in America a rapid method has been introduced by Morey* whereby the stirring is performed during the melting and fining process and commenced as soon as the glass is present in sufficient amount to half fill the pot. It is claimed that by so doing melting is expedited and pot attack is diminished.

(369) **The Stirring of the Glass.**—Now comes the important operation of stirring, whereby a glass as homogeneous as possible may be obtained. This process is accomplished by a suitable machine, consisting of a fireclay cylinder maintained in a vertical position in the metal and kept in motion by means of an iron stirring rod. The fireclay cylinder itself is rather more than two feet in length, being, in the case of open pots, a little shorter than the height of the pot (thus a 27-inch pot would have a cylinder about 26 inches long). Its external diameter at the top is about 4 inches, tapering to about 3 or 3.5 inches at the lower end. At the top is a circular rim or flange an inch deep and projecting about the same distance from the main body; this rim serves to support the cylinder against the edge of the pot when not held in position by the stirring rod. An opening some seven inches long runs down the cylinder from its upper end, into which the holding pin of the stirring rod just fits, and, that no slipping may occur, the hole is sometimes made square in section in its upper four inches, to correspond with a similarly shaped portion of the holding pin. Before it can be used, the cylinder, which is made out of fireclay in the ordinary way, is first carefully dried, and then brought up to the temperature of the glass itself, when it is taken from the pot-arch and placed in the pot of molten metal.

The stirring rod is water-cooled. It is fixed horizontally to pins situated eccentrically on the upper faces of two circular discs, which are mounted on the frame of the stirring machine, and are capable of being rotated in the same horizontal plane by a motor (*see* Fig. 227). This machine is provided with wheels, and it can be run into position before the furnace, so that the far end of the rod projects through the stopper-hole and over the pot. At its extreme end the stirring rod is bent at a right-angle, the vertical extension being capped by the holding pin already mentioned, for engaging the fireclay cylinder. When the pin has been fitted in the socket, the motor is started and the rod is thus so moved that the fireclay cylinder performs a horizontal stirring motion in the pot. The size of the circles performed by the stirrer is governed by the position of the pins on the rotating discs, and these allow of adjustment. Stirring is so regulated by an independent movement of the machine that every region of the glass is disturbed except that close to the sides, since in the latter case heavy veins would be drawn into the mass. In some types of stirrer an independent vertical

* *J. Amer. Cer. Soc.*, 1919, 2, 147.

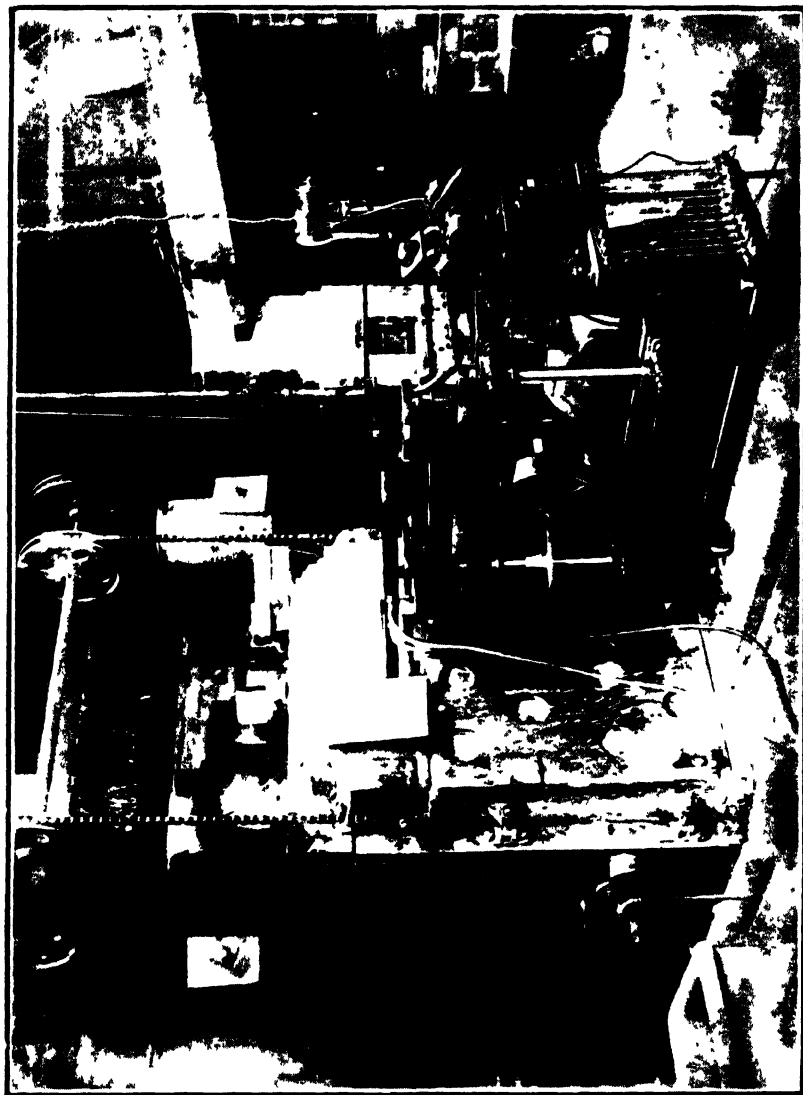


FIG. 227.—A MACHINE FOR STIRRING OPTICAL GLASS
(By courtesy of Dr. J. W. French, Messrs. Barr and Stroud, Ltd., Glasgow.)

motion can be given at the same time to the stirring rod, to ensure the mixing of horizontal layers of metal, a precaution only necessary in the case of heavy lead glasses. The rate of stirring depends, of course, upon the kind of glass which is being manipulated, but it varies roughly from 12 to 16 revolutions per minute. It is inevitable that when the stopper is removed, to allow of the introduction of the stirring rod, a drop in temperature will be caused, but this should not be more than about 50°C. , after which the temperature is maintained as steady as possible during most of the stirring operation. After each stage of stirring the temperature is raised just sufficiently for any gas-bubbles that have been evolved to rise to the surface, but not enough to cause convection currents. These gas bubbles are a constant source of trouble, and may



FIG. 228.—A POT OF OPTICAL GLASS AFTER COOLING.

(By courtesy of Dr. J. W. French, Messrs. Barr and Stroud, Ltd., Glasgow)

arise in a number of ways. Many of them, of course, are due to gas liberated in founding and only slowly evolved, but others may be dragged in mechanically by the stirrer itself, whilst trouble has also been caused by water drops leaking from an imperfectly sealed joint between the stirring rod and the holding pin welded to its extremity.

Should, now, the period of planing and mixing be complete, it is necessary to cool the pot somewhat before removing it from the furnace. To this end, the gas is cut off, without, however, chilling the furnace too suddenly. Soon, the glass becomes more viscous, and as it cools, the rate of stirring is reduced to a degree only to be gauged by experience. When cooling has reached the requisite stage stirring is stopped, the stirrer is removed, and the pot of fluid glass is lifted from the furnace in order to quickly cool and so solidify the layer of glass at the bottom and sides.

The temperature at which stirring is stopped is of the greatest importance, since upon it depends whether or not striæ will appear in the glass. In some cases, in order to chill rapidly, the pot is even sprayed with water for a short time. At this point the pot is placed into the pot-arch, which has been suitably heated (not too hot, since this would melt the glass, so producing unevenness), and allowed to cool at a slow, carefully regulated rate. Some glasses may be cooled upon the floor of the furnace room, without becoming excessively broken up, whilst certain types are even poured upon casting tables and rolled out like plate glass.

Melting and fining, with subsequent stirring, up to the stage of removing the pot from the furnace usually takes 20 to 24 hours, a convenient time in regard to the normal factory hours of work.

(370) **Breaking-up and Moulding the Glass.**—When the pot is cold it is broken open and the glass in it is found to be broken into many pieces (see Fig. 228). Providing that cooling has been satisfactory, a number of fairly large lumps, reasonably rectangular in shape, are obtained. These lumps are examined for faults, such as striæ, stones, and bubbles (no accurate judgment can be made at this stage, however), and defective portions are broken off, the pieces being hand-chipped to the calculated weight of the plate or block it is desired to mould. These pieces are now placed in gas-fired furnaces and brought nearly to the softening point, when they are put into suitably sized moulds in a special softening furnace and pressed into the desired shape.

Some firms perform moulding in one furnace, tunnel-shaped, and heated at one end. The moulds containing the cold slabs are placed in the cold end of the furnace and gradually moved to the hot end, when the glass softens and flows into shape. Square or rectangular slabs are formed by the moulding process, these being allowed to cool slowly to give a rough annealing.

(371) **Examination of the Glass.**—Opposite ends of the slabs are now ground with carborundum and polished with rouge, when a careful examination is carried out, faults visible with the naked eye—*i.e.*, striæ, moulding faults, stones, or large bubbles—are noted, and the defective pieces rejected.

(372) **The Final Annealing.**—Those slabs which have been accepted are given a "fine" annealing by heating up to the annealing temperature and very carefully cooling over a period of several weeks. There are two types of annealing furnace, and both are electrically heated. In one type the glass is packed in trays in a furnace which is a well insulated box of refractory material, capable of holding about 600 lb. of glass. In the second type a lehr arrangement is used, and the glass, contained in circular metal boxes, passes slowly and regularly down an electrically heated tube having a predetermined temperature gradient. Electrical heating is employed because of the perfect temperature control which it allows.

(373) **The Making of Lenses.**—We may conveniently conclude our description of optical glass manufacture with a summary of the methods of cutting, grinding, and polishing the glass to produce lenses.

CUTTING.—This is performed on a wheel of about 15 cms. radius composed of soft iron or bronze and revolving at about 350 revolutions

per minute. The edge of the wheel is levelled and lightly nicked, and on to it is brushed diamond dust ("bort") to serve as a cutting medium. During cutting, lubrication is obtained by means of soda-water or soap-suds.

GRINDING.—After cutting into pieces somewhat larger than the lenses to be made, the glass is ready for grinding. Surfaces are ground either plane, spherical, or cylindrical (*i.e.*, curved in one direction only). In order to obtain the desired shape the blanks are fastened upon a circular iron table, **8** (Fig. 229), having exactly the radius of curvature desired for the surface of the lens. Thus for a plane surface a perfectly flat disc is used; for a concave surface the disc is suitably hollowed; for

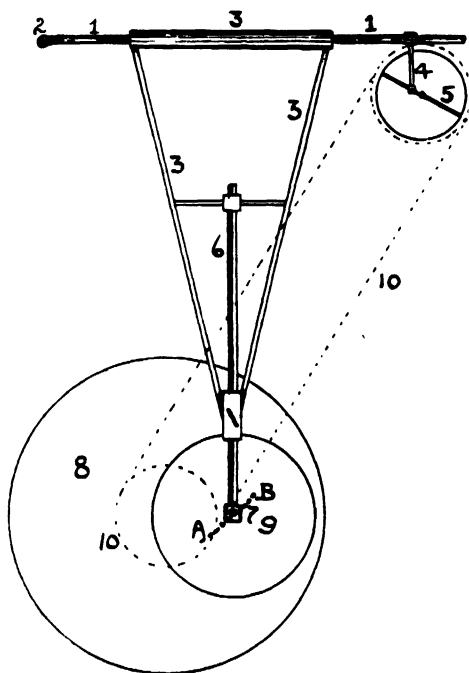


FIG. 229 —A GRINDING AND POLISHING MACHINE FOR OPTICAL GLASS.

a convex surface it is crowned or somewhat dome-shaped; finally, for the production of cylindrical lenses a surface curved in one direction, but flat in a direction at right-angles to this, is employed.

To this table as many blanks as possible are carefully and evenly fixed by means of Swedish pitch. The table is now placed upon a central vertical spindle, rotated below by a belt and pulley drive, **10**. As a grinding tool, a cast-iron disc, **9**, made with exactly the same curvature as the table beneath it, is used. This tool is held by a pin, **7**, fastened at the end of a horizontal arm, **6**, which is again held in a triangular frame, **3**. The remote, short side of the triangular supporting frame is composed of a tube which slides upon an iron bar, **1**, and can be clamped

upon it in any desired position. One end of the bar, **1**, is pivoted (at **2**), whilst the other can turn freely in a horizontal direction. An adjustable arm, **4**, pivoted at the point of its attachment to the bar, **1**, is fastened at its further end by a pin, which can be clamped at any desired point in a diametrical slot in the horizontal disc, **5**. The disc rotates upon a central supporting spindle which can be driven at any desired rate from a main power-shaft, either by a belt and pulley or a friction drive. It is from this spindle that the table, **8**, is driven.

Imagine, now, the whole instrument set in motion. Table **8** will rotate at a uniform rate, whilst the bar, **1**, will have a reciprocating motion around its fixed end. This means that the grinding tool, **9**, will pursue a curvilinear path, **A-B**, over the face of the table, its weight pressing upon the lenses beneath. The length of path which the grinding tool takes is decided by the position of the pin in disc **5**, for the further this is from the centre, the longer will be the angle of oscillation of the bar **1**, and consequently of that of the driving arm, **6**.

Emery of varying grades of fineness is fed on to the table, beginning with coarse and gradually becoming finer as the process continues, whilst water is also run on to the surface of the glass. Grinding is continued until the glass is shaped and smoothed.

POLISHING.—The operation of polishing is performed in the same manner as grinding, but by means of rouge and water. Careful regulation of the amount of liquid present is necessary both for grinding and polishing. When one side has been finished, the lenses are removed, reversed, and stuck upon another suitably curved tool, when the second surface is ground in the same way as the first.

SHAPING.—Having ground the faces of the lens, the glass is roughly shaped with special soft irons (shanking irons), by means of which portions of the edge are broken off until the desired shape is approximated. A number of lenses are then stuck together, face to face, with a resin-beeswax cement, and the cylinder so formed is ground to shape. Afterwards, by warming the cylinder, the cement is softened and the finished lenses are separated.

For spectacle and similar lenses (generally made of ordinary fairly cheap types of glass) a number of bevelling machines for edge grinding have been patented.

CHAPTER XXXVIII

THE PRODUCTION OF HOLLOW WARE

I. Fashioning by Hand.

(374) **Definition.**—The term “hollow ware” is self-explanatory. We may include in this section two classes—namely, pressed ware and articles (apart from bottles and window glass) made on the pipe by the actions of marvering, blowing, etc. We have already discussed machinery for pressing glass; we now turn to the hand processes employed in producing hollow ware, and to the means adopted for the decoration of glass, the two forming together a distinct branch of the industry.

As a detailed description of the whole of the so-called “flint” glass manufacture would be impossible, we shall be content merely to indicate the tools and processes chiefly employed, and to give a fairly detailed account of the manufacture of a few standard types. In conclusion, the main decorative processes will be considered.

(375) **The Kinds of Glass Used.**—For the type of ware under discussion appearance is a prime factor. Much of the glass employed is of the lead crystal type, since not only does this glass possess a characteristic brilliancy, but it generally gives better colour effects than does soda-lime glass. Again, it is a simpler glass for shaping, remaining longer soft and workable on the pipe. Finally, it is the best glass for cutting and engraving. Although possessing the foregoing advantages, lead glass is by no means universally used for making hollow ware, since considerations of price tell against it, whilst the effects obtained by the use of good soda-lime, or, better still, potash-lime or potash-soda-lime glasses are by no means to be despised.

We may here again stress the need for the use of pure materials, since no amount of manipulative skill will atone for the deficiency of a glass of poor appearance. Glass required for hollow ware must also be carefully melted and fined, so that not even small stones and seed are present. Most of the melting is performed in pot furnaces, and, where lead glasses are concerned, in closed pots, but we have already pointed out cases where small tanks are employed for certain of the glasses needed for this work.

(376) **The Tools Employed.**—Working may be performed on the pipe either at the chair, using various tools, such as tongs and shears, or it may be accomplished by the use of moulds, whilst a combination of the two classes of work is not uncommon. Of tools used for “chair” and mould work the following may be detailed.

THE PIPE.—Very generally, a pipe of iron about a yard in length, a half to two-thirds of an inch in diameter is employed. A wooden

sleeve or handle slipped over the pipe at a point remote from the nose helps in manipulation.

THE CHAIR.—This has previously been described. The *marver* and *punty* also need no further discussion.

THE SHAPING BLOCK.—In order to obtain an even, symmetrical globe or bulb as a parison, so that the finished article shall be of uniform shape

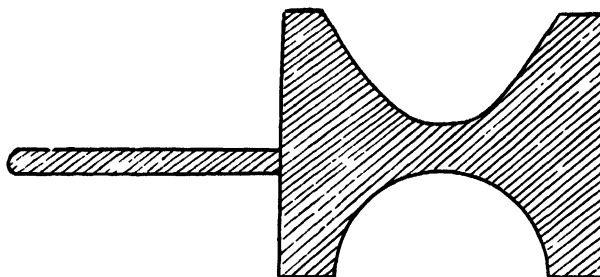


FIG. 230.—A SHAPING BLOCK.

and thickness, a shaping block is regularly employed. This consists merely of a block of wood in which is a hollow for the reception and rotation of the parison. Two shapes of hollow are used, a hemispherical recess and a conical one, the former for obtaining a globular parison, the latter for making tapered articles such as tumblers. Fig. 230 illustrates a shaping block possessing both hemispherical and conical recesses.

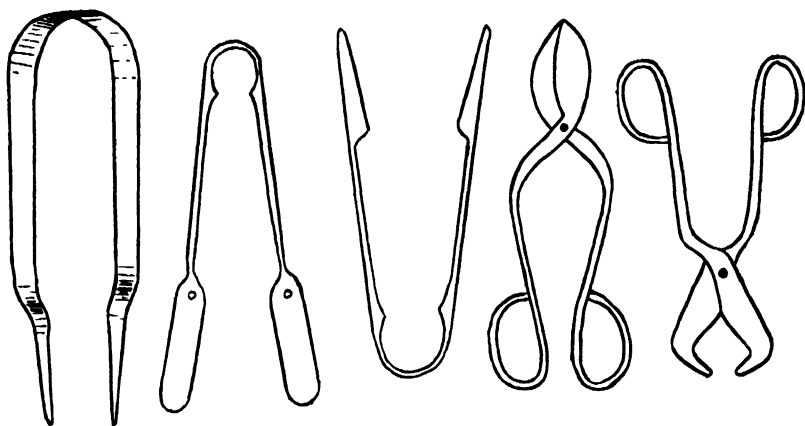


FIG. 231.—TONGS AND SHEARS.

TONGS.—Iron tongs of various shapes and for differing purposes find wide application. Several types are shown in Fig. 231. One form, having pointed ends, is used for smoothing and flattening the sides of the parison, opening the neck, etc. All these processes are performed by holding the tongs against the soft glass and rotating the pipe on the arms of the chair. A tool sometimes used for flattening the foot of a

wineglass consists simply of two flat pieces of pear-wood hinged together so that the glass can be pressed between them (Fig. 232).

SHEARS.—Two common shapes for shear blades are shown in Fig. 231.

MOULDS.—Wooden moulds, made by turning or chiselling, may be employed for shaping some forms of hollow ware. They possess the disadvantage that they slowly burn away, and objects made in them are of a gradually increasing size. Consequently, when articles have to be made rigidly to size, wooden moulds are inadmissible. The utmost life of a wooden mould allows of probably not more than a thousand articles being shaped in it, and only then when these are fairly thin-walled. Only woods giving a soft charcoal may be used for moulds, since, when a hard, glassy charcoal is formed on the surface, the latter becomes uneven and rings are formed. Suitable woods are lime, poplar, and alder. Wooden moulds possess the advantage that they do not destroy the smooth, polished appearance of the glass surface touching them—that is, the so-called “fire polish.” In order to secure maximum evenness and polish, the pipe is rotated whilst the parison is held in the mould, unless the shape renders this impossible. It is usual to make

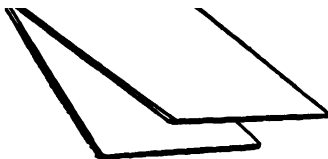


FIG. 232.—WOODEN FLATTENING TOOL.

wooden moulds in one or two pieces, and in the latter case the parts are hinged together. Moulds of wood are sometimes made without a bottom.

Carbon moulds are similar to wooden ones, in so far as they allow of the retention of the fire polish, whilst they are also more durable than wooden moulds. They are prepared by pressing a mixture of powdered gas carbon and tar over a wooden model until a layer of sufficient thickness is obtained. The mould so formed is cut into two and heated to vaporise the binding material. A wooden case or holder then serves to receive the mould, and it is ready for use.

METAL MOULDS.—Very commonly, cast-iron moulds are employed. They last much longer than do moulds of wood or carbon, but they have the great disadvantage that they largely destroy the fire polish on the surface of the glass, although for cheap ware this is no great detriment. In order to overcome this difficulty, “paste moulds” may be used. These are cast-iron moulds, the inner or shaping surface of which is coated before use with the so-called “paste,” a material which, when heated, gives a layer of carbon over the surface of the mould. A paste mould consequently combines the advantages of a carbon mould with those of a cast-iron mould. In use, the parison is rotated in the mould, and so mould marks (formed at the junction of the halves of the mould) and surface unevenness are prevented.

The following methods of preparing a paste mould have been described: (a) Finely ground charcoal and resin are mixed, spread on the mould and smoothed out evenly by a gathering of hot glass. (b) The mould surface is warmed, a coat of linseed oil or thick varnish is spread on, and very finely ground charcoal evenly sieved over. (c) Equal parts of varnish and resin are melted together for one or two hours, and then one-third as much red lead is mixed in. With this mixture the mould is evenly coated and then fine charcoal is sieved over it. Before use, the mould is left standing for several hours, or else heated at the furnace. Paste moulds are extremely difficult to prepare successfully, the method of coating being as important as, or even more so than, the composition of the paste itself.

For certain classes of work, particularly surfaces with designs in high-relief, brass moulds may be employed, whilst of recent years moulds of an iron-nickel alloy and of aluminium have come into use.

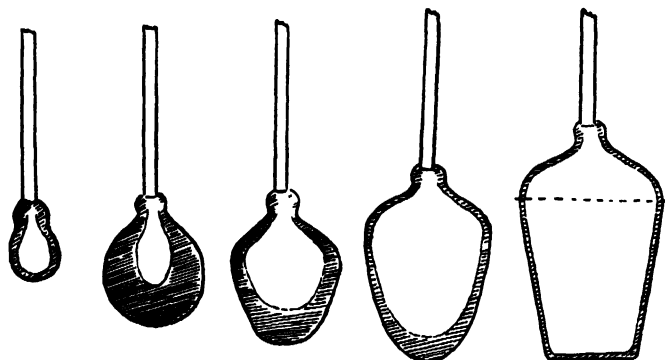


FIG. 233.—MAKING A TUMBLER.

OTHER TOOLS.—In addition to the above, special iron and wooden tools for cracking off, shaping the lips of vessels, and other specific purposes are employed, the shape of which largely depends on the kind of articles manufactured.

(377) **Making a Tumbler.**—The glassblower's assistant first dips the nose of the pipe into the molten glass, rotates it to gather a small amount of metal, and by marvering and blowing shapes this into a small bulb (Fig. 233). On the bulb so formed is now gathered more glass until sufficient has been obtained to form the desired tumbler. By first making a small bulb in this way and using this to gather upon, the metal is kept well in front of the nose of the pipe. The pipe is now rotated on the arms of the chair, and by means of the tongs a groove is pressed in the neck of the parison close to the nose of the pipe, where, later, cracking off takes place. In order to ensure evenness of the walls of the bulb, the parison is lowered into the hemispherical recess of the shaping block, and the pipe carefully rotated. The shaping block is now reversed and the parison rotated in the cone-shaped hollow, whereby it is given suitably tapered walls. The "maker" himself now takes over the pipe, reheats the parison, if necessary, at the working hole, and

by swinging and blowing enlarges it evenly both in length and in breadth. When sufficiently large the parison is pressed upon a flat surface and the bottom so shaped.

Should it be desired to finish the tumbler by hand, the assistant next gathers a small amount of glass on a punty and sticks this to the bottom of the vessel. The pipe is now cracked off by moistening the constriction, in order to form a circular crack, and giving the pipe a sharp blow. Holding the glass by means of the punty, the mouth of the tumbler is heated in the working hole, and, when soft, is cut to size with the shears. A further reheating of the mouth allows of it being pressed into shape with a wooden shaping tool or the tongs as the pipe is rotated on the chair. The tumbler is now placed in the lehr.

More generally, nowadays, after the tumbler is shaped it is cracked from the pipe, annealed, and the cap removed by means of a suitable cracking-off machine.

(378) **Making a Fluted Lamp Shade.**—Glass is gathered on the pipe, blown into a small bulb, and subsequent gatherings taken upon this until sufficient material is present to give the desired globe. Careful shaping

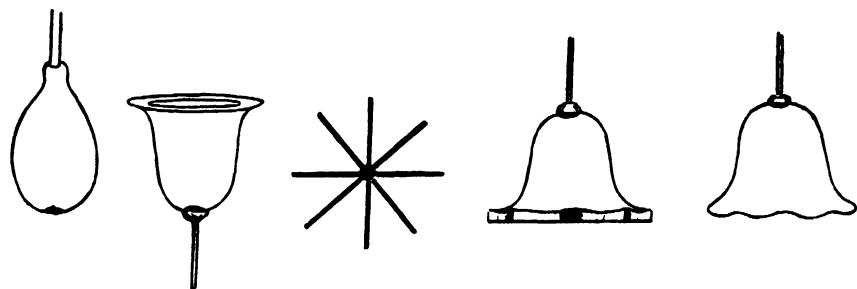


FIG. 234.—MAKING A FLUTED LAMP SHADE.

and blowing now gives a large bulb, the lower half of which is approximately of the shape of the upper portion of the shade. A piece of molten glass applied to the end of the bulb remote from the pipe now serves to soften the glass so that a hole can be blown at this point, and the hole is further cut to a circular shape with the shears (Fig. 234). This completes the upper portion of the shade, the circular hole later serving to attach the finished shade to the lighting bracket. A punty with a gathering of glass is brought by an assistant to the open end and there attached, after which the pipe is cracked off. The end cracked from the pipe is now reheated and cut well open with the shears. After further reheating this end is opened out with a wooden shaping tool and a horizontal flange is made at the edge. The flanged end is reheated until sufficiently soft, when the punty is held vertically over a moulding tool standing upon the floor. This tool consists of a number of thin iron bars or sheets radiating from a centre and held in position by a fireclay or other frame. The punty is held directly over the centre of the mould and lowered until the flanged portion of the glass just touches the radial bars. In this way the glass touching the iron is chilled and stiffened, whilst that between remains soft and sinks somewhat. At the

correct time, the punt is rapidly raised and swung in the hands until the flange has fallen into the required position. If done correctly the intermediate, soft portions of the flange will fall more than those parts which have been chilled, and a regular fluting is obtained. The shade is now finished; it is cracked off from the punt and placed in the lehr. If the glass contains an opalising medium, such as bone-ash, or a ruby-producing element (*e.g.*, selenium, copper, or gold), the reheating of the flange renders the fluted portion opal or red, as the case may be, whilst the body of the shade remains colourless.

(379) **The Production of Ribbed or Fluted Ware.**—A similar device to that for producing fluted edges is employed for the production of vertical ribs in glassware. A circular mould of sheet-iron, 6 to 12 inches in height, contains a number of radial sheet-iron projections. On blowing the parison in such a mould the side of the glass becomes ribbed (Fig. 235), a decoration retained even in the after working of the glass in other moulds. A pretty effect is obtained by first fluting the parison in this

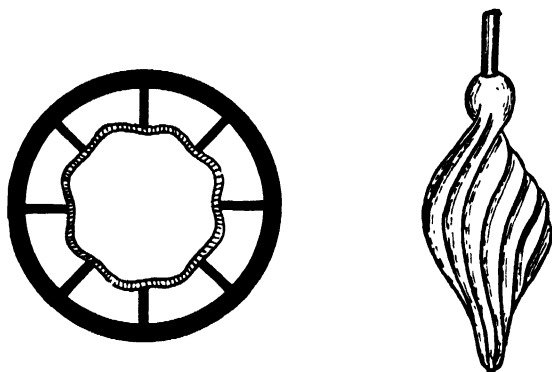


FIG. 235.—THE PRODUCTION OF RIBBED WARE.

way, seizing the tip with the tongs (after withdrawing the glass from the mould), and then rotating the pipe. By this means a spiral fluting is obtained as indicated in Fig. 235.

(380) **Making a Jug.**—The upper portion of this vessel is made in a wooden mould (Fig. 236). The glass is gathered, marvered, and then blown to shape in the mould. At the same time a second workman gathers enough glass to make the base of the jug and blows this to shape in a second mould. Whilst the base is rotating in the mould a lehr-boy rings it round deeply and smoothly with the tongs close to the mould, to facilitate the later process of cracking off. Upper and lower parts are held in the furnace to soften and then pressed together. To complete the mouth of the jug the upper pipe is first cracked off around the ring **A B** with a moist iron, and the opened end held by means of the second pipe in the working hole. When soft, the top is opened out with the tongs, reheated and hollowed in two places with the shears in such a way as to leave a projecting portion. This projecting portion is then pressed out into the form of a lip by the tongs or a shaping tool (Fig. 237).

To form the handle, an assistant takes a quantity of glass on a punty and marvers it into the form of a long cylinder. This is held vertically and the jug placed horizontally below, so that the lower end of the cylinder adheres to the wall of the jug close to the rim at a point diametrically opposite to the lip. The cylinder is pressed until it unites with the jug at this point. The glassblower now takes the pipe, which holds the

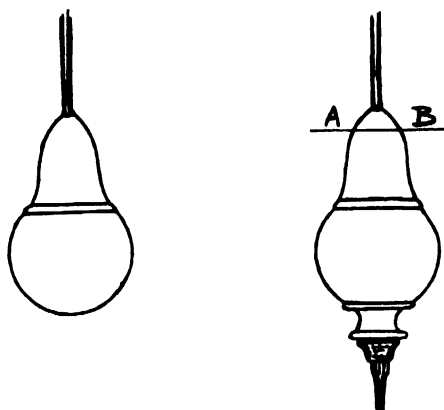


FIG. 236.—MAKING A JUG (BODY AND FOOT).

jug, in his left hand and cuts off with his right sufficient glass from the cylinder to give the handle. He presses the severed end against the jug at the point desired for the lower junction of the handle, and finally, whilst the handle is still soft, shapes it with the tongs. It remains now only to crack off the jug from the pipe at the constricted point and place the finished article in the lehr.

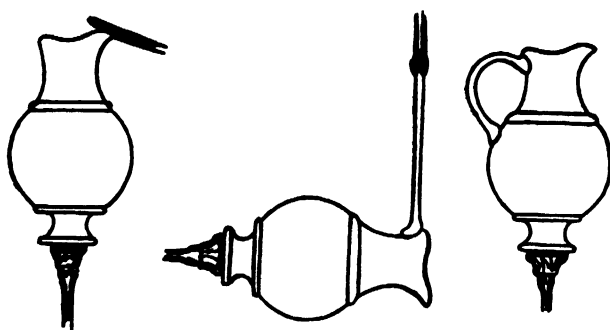


FIG. 237.—MAKING A JUG (LIP AND HANDLE.)

(381) **Making a Wineglass.**—Upon the pipe is first gathered sufficient glass to produce the bowl of the desired vessel. This is marvered and blown until of the requisite size and shape (Fig. 238, 1 and 2). The pipe is now held vertically and, from a punty, sufficient glass is run upon the bowl to form the stem, (3), a process necessitating accurate

and careful adjustment of both position and amount. Resting the pipe on the arms of the chair and rotating it continuously with his left hand, the workman shapes the still soft stem with a pair of tongs, (4), after which the glass is sufficiently set to receive the foot. Again the glassblower holds the pipe vertical, and molten glass is run on to the end of the stem, (5), until sufficient is present to form the foot of the glass. At this point the pipe is once more laid across the arms of the chair and, whilst it is rotated, an assistant presses a flat piece of wood against the foot, (6), so roughly shaping it. The final shaping is performed by the glassblower himself, (7), by means of the tongs, whilst still keeping the pipe in rotation. In order to sever the wineglass from the pipe, a punty is first attached centrally to the foot of the vessel, (8), by a small gathering of glass, and the bowl is then cracked off at the desired point by a moist iron, after which a sharp blow frees the glass from the pipe, (9). There remains the shaping of the rim. For this purpose the raw edge of the bowl is reheated at the mouth of the furnace, is cut to shape with the shears, (10), and is finally flanged by a wooden tool, (11), as the punty is rotated on the arms of the chair. The finished glass, (12), is severed by a blow from the supporting punty and rests on a suitable table until carried on a fork to the lehr.

(382) **Spun Glass Decoration.**—Very effective results may be obtained by spiral line designs in glass thread upon the surface of glassware. This process is most simply carried out as follows. Whilst the article to be decorated is being blown a gathering of glass is taken on a punty and marvered into the shape of a cylinder with a pointed end. Then, whilst an assistant rests the pipe horizontally in a fork and evenly rotates it, the glassmaker first touches the ware at one point with the tip of the cylinder, whereby a junction of the glasses is made and the cylinder pulled out into a thread. By holding the punty just below the ware and moving it regularly in a horizontal direction as the pipe rotates, an even spiral line of glass thread is laid over the glass surface.

For more even results a spinning machine (*see* Fig. 239) is employed. It consists of a simple lathe with a hollow spindle in which the pipe can be held. The forward end of the spindle is threaded and engages in a thread in the bearing. Thus on rotating the spindle it is driven evenly in a horizontal direction. The motive power is by hand through a belt and pulley drive, and to allow of the movement of the spindle the belt pulley upon this is free to move horizontally, being held by a pin running in a horizontal slot in the spindle. To operate, the pipe with the article attached is placed in the spindle, a cylinder of glass is obtained, and contact made as before. It is then only necessary to hold the punty still whilst the machine is driven regularly to obtain the desired result.

(383) **The Casing and Flashing of Glass.**—In making articles of coloured glass it is often found desirable to have the colour as a thin surface coat or casing over an inner layer of colourless glass, or sometimes, again, the coloured glass may be sandwiched between two colourless layers.

These methods of treatment are necessary when the colour is very intense, particularly with cobalt blue or ruby glasses, for if the whole article were composed of such glass, and a deep, rich tone were desired,

the thicker portions would be practically opaque. Very beautiful effects are also obtained by "*flashing*" the surface of a crystal glass with a coloured layer, and then either cutting or etching a design upon the glass. By this means the decoration is picked out in colourless glass upon a coloured background. A still further modification is to flash two or more layers of different colour upon the crystal glass, and then to cut a design, in which case delightful variations of colour and tone can be obtained by cutting to different depths.

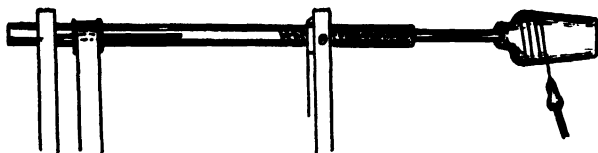


FIG. 239.—SPUN GLASS DECORATION.

(384) **Casing from the Pot.**—One method of producing an outer casing of coloured glass lies in the provision of a pot of coloured metal in close proximity to the pot of crystal glass. A gathering of the latter is taken upon the pipe in sufficient amount to produce the desired article, and this is blown into a bulb. The bulb is now dipped into the pot of coloured metal and rotated until a coating of requisite thickness, and as even as possible, is obtained. This parison is finally removed, blown and formed in the ordinary way. To produce an inner coloured layer a small bulb of colourless glass is first blown and dipped into the coloured metal. A further gathering of crystal glass is afterwards made until the whole is of sufficient amount to give the desired object when the glass is worked as usual. When a coloured layer of varying thickness is required it may be obtained in the following way. A bulb of crystal glass is first blown and a gathering of coloured glass made upon it. By

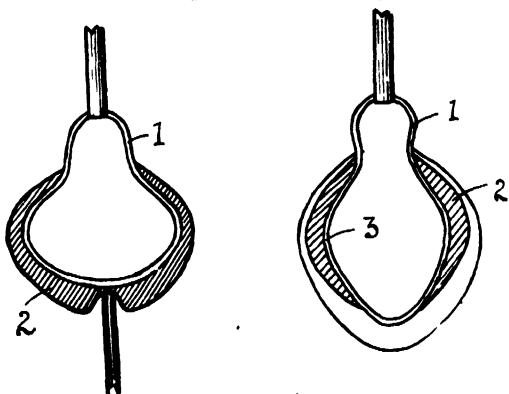


FIG. 240.—CASING FROM THE POT.

piercing the coloured layer at the tip of the bulb with an iron it is thinned at this point (Fig. 240). The bulb is now blown slightly larger, after which an outer gathering of clear glass is made, giving thus an inner ring of coloured glass, thicker in the middle and tapering towards the top and bottom. Blowing and forming now give an article in which the colouring is not even and variations of tone result.

(385) **The Use of Coloured Rod.**—Where a number of colours are desired it may not be feasible always to keep the requisite pots of coloured glass. In this case, at some convenient time when the furnaces are at

liberty, the coloured glasses are made and worked into rods, 10 to 12 inches long and about 1.5 inches in diameter, which are carefully cooled, stored, and used as desired. When flashing is to be done, a piece of the rod is broken into two approximately equal portions and laid on a moulding stone near to the furnace that it may become warm. Gradually one of the pieces is moved nearer to the furnace until it is sufficiently hot to be attached to the end of an iron by means of a small gathering of glass, when it is held in the working hole to soften. Meanwhile a gathering of colourless glass has been made, blown into a bulb and allowed to cool until it is no longer soft. It is now supported in a horizontal position close to the furnace and the softened piece of coloured metal pressed

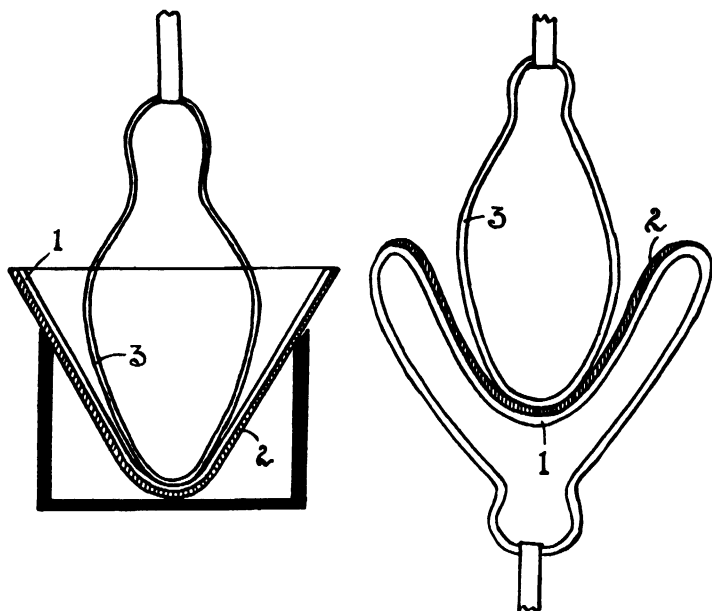


FIG. 241.—FLASHING BY THE "FUNNEL" METHOD.

against it until the bulb has passed half-way through the rod. The latter is spread out somewhat, cut close to the bulb with shears, and excess material removed for future use. By holding the parison in the furnace until it is workable the coloured glass can then be evenly spread over the surface with a wooden moulding tool. Further working is as by the former method. Production of coloured cane for casing is now a distinct trade, and some firms supply glass for this purpose in a series of definite colours and shades, and of uniform coefficient of expansion.

(386) **Flashing by the "Funnel" Method.**—To obtain a thin, even layer of coloured glass for cutting or etching, the above methods of casing would not be suitable, and two modifications are employed. The first is the so-called "funnel" method. In this a sufficiently large bulb of

crystal glass is first blown and cased as before. This bulb is blown to its greatest extent and its tip attached to a punty, when it is cracked off from the pipe. The open end is now widened as far as possible, giving a funnel-shaped body from which the punty is detached. A wooden stand now serves to hold upright this funnel of glass, into which is suspended and blown a crystal glass bulb (Fig. 241). To accomplish successfully the junction of globe and funnel, the tip of the former only is allowed to come into contact with the funnel at first, at the very bottom; when contact is made, slow and gradual blowing seals the sides evenly towards the top, and so prevents the inclusion of air bubbles.

By the second method, a bulb of sufficient size is made and the lower portion covered with coloured glass, after which the bulb is blown out. It is now strongly heated to fully soften the half which is cased, and the pipe is held vertically in order to allow the softened portion to sink inwards (a process assisted by the workman sucking air through the pipe). This bulb is cracked off from the pipe and treated as if it were

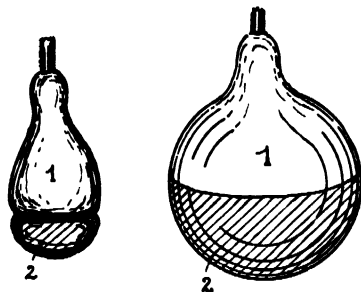


FIG. 242.—SEMI-CASED GLASS.

a funnel, with the exception that only the coloured wall, 2, is allowed to remain on the second bulb, a process accomplished by sprinkling the clear glass layer, 1, with water and so cracking it off.

(387) **Semi-Cased Glass.**—For illuminating ware in particular it is often necessary to produce a globe of which only the half is cased. For this purpose a bulb of colourless glass is first blown and its end is flattened. On to this flat end is now carefully placed sufficient coloured glass to produce the casing (Fig. 242), a clean junction of the two glasses being essential or the dividing line will later be uneven. Further blowing now suffices to produce a globe with its lower half cased. For this type of casing opal glass is largely employed.

If it is desired to case the upper half of a globe, with the opening at the top, a more difficult problem is presented. In these circumstances the following method is found suitable in practice. By means of a mould, a cylindrical tube of coloured glass of somewhat smaller diameter than the desired article is prepared. After cooling, the cylinder is sprung into rings of a height equal to the depth of the desired casing. One edge of each ring is now ground and smoothed. To attach the ring to the colourless glass it is first heated very strongly and slipped into a recess in the upper half of a suitable mould (see Fig. 243), in which the colour-

less parison is blown; to the latter the softer coloured ring adheres. Strong heating serves to soften the whole and to produce a perfect union between the two glasses, after which the parison is placed in a finishing mould and blown to shape.

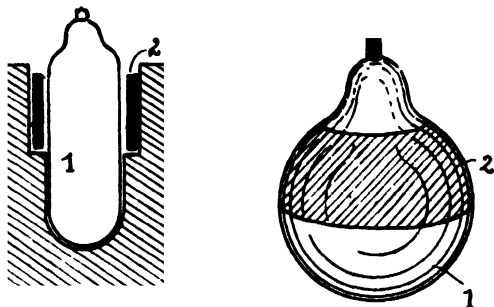


FIG. 243.—SEMI-CASED GLASS.

(388) **Unsymmetrical Casing.**—It is sometimes desired to cover the upper portion of a globe with coloured glass, but to produce a sloping line of junction between upper and lower portions. In this case a bulb is first made of coloured glass, and, whilst it is soft, a hole is cut somewhat to one side (Fig. 244). Over the coloured glass is now gathered the necessary amount of colourless metal, and the parison blown and finished. A result as illustrated in Fig. 244 is obtained, the casing here being on the inner side of the finished ware.

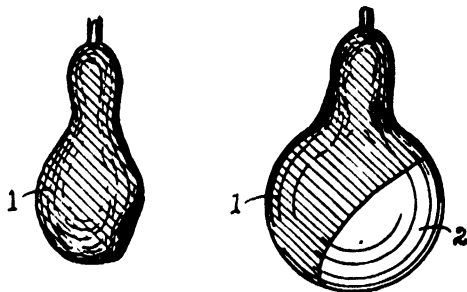


FIG. 244.—UNSYMMETRICAL CASING.

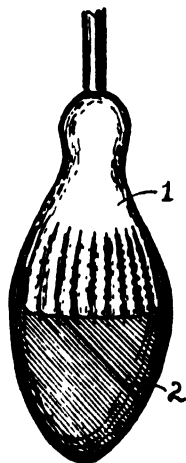


FIG. 245.—THE PRODUCTION OF A WAVY JUNCTION.

(389) **The Production of a Wavy Junction.**—A colourless glass bulb is first blown with pronounced vertical ribs. The bulb is further warmed and blown and the outside smoothed. By flattening the end of this bulb and placing on it a gathering of coloured glass a result is obtained similar to that shown in Fig. 245. At this stage, however, the parison is elongated by swinging, in which process the thickened ribs lengthen

less rapidly than the thinner wall between. As a result an uneven, wavy effect is obtained at the junction of the two glasses.

(390) **Adjustment of Coefficients of Expansion.**—We have indicated in the chapter on physical properties how important it is in the successful casing of glassware that the glasses should have approximately equal coefficients of expansion. The matter should be regularly checked, and since calculation is not easy the following method, suggested by Hovestadt and also by D. E. Sharp,* will be found useful in practice. Two rods, one of each of the glasses it is desired to unite, are placed side by side with the ends flush. After heating the ends and pinching these together with forceps, so as to weld the glasses, the welded portion is drawn out into a

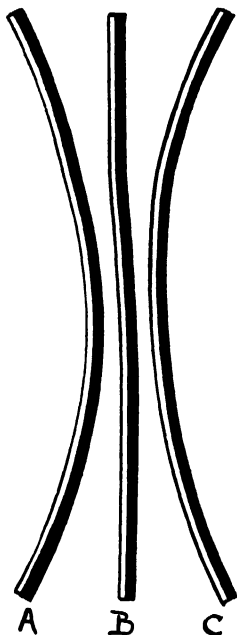


FIG. 246.—THE ADJUSTMENT OF COEFFICIENTS OF EXPANSION.

thin strip, of which the two original glasses form opposite sides. When cooled the strip will be found to bend towards the glass having the higher total expansion up to the softening point of the softer glass, as at **A** and **C**, Fig. 246. A very slight curvature of the strip (or none at all, as at **B**) indicates that with careful annealing a satisfactory junction could be made, which is not the case if the curvature is appreciable.

Another method consists in preparing a cylinder of cased glass about two inches in diameter and splitting it into rings. These rings are split open longitudinally, when, if the two expansion coefficients are approximately equal, the severed edges remain fairly close together. If the edges pull fairly far apart or overlap considerably the two glasses are unsuitable.

* *J. Amer. Cer. Soc.*, 1921, 4, 219.

CHAPTER XXXIX

THE PRODUCTION OF HOLLOW WARE

II. After-treatment and Decoration.

IN the preceding pages the handworking of glass, as related chiefly to artistic glassware, has been dealt with briefly. The following section presents a short description of methods, mainly mechanical, employed for the finishing of the handworked product and for its final decoration.

(391) **Cracking-off Machines.**—Tumblers and similar hollow ware, after blowing, require the dome-shaped cap to be cracked off at a suitable height from the base. Provided that the ware is sufficiently thin-walled, the following simple apparatus is quite effective for this purpose.

Three small circular iron tables, supported at exactly the same height by vertical spindles upon an iron framework, serve to hold the articles to be treated (*see* Fig. 247). The two outer tables can be rotated mechanically by belt and pulley drives, but the central table is turned by hand. Against each table is a vertical pillar, the central one of which carries a diamond capable of being clamped at any desired height above the table. On each of the outer columns are clamped two horizontal burners giving fine-pointed flames. The flames are so arranged as to be at exactly the same height as the diamond and to play upon opposite sides of the glass standing on the table beneath. In practice, the article from which the cap is to be cracked is placed upon the central table touching the diamond, and rotated once so as to give a scratch completely around it at the required height. It is then placed upon one of the rotating tables and left with the flames playing exactly upon the scratch until the glass at this point is hot, when the article is removed and the hot ring moistened, whereby the cap evenly cracks off. Whilst the first glass is being heated a second is scratched and placed upon the other heating table, the one diamond being sufficient to serve both pairs of burners. Success in this operation depends upon the correct adjustment of diamond and burners, and upon the fineness of the heating flame.

In a modification of the above apparatus the diamond and burners are immovably fixed at the same height, and adjustment for the height of the objects to be cracked off is obtained by raising or lowering the three tables simultaneously by the rotation of a single screw. Fig. 248 illustrates a more completely automatic form of machine, made for greater production, the patent of C. Melin and Co. A series of holders are set on the edge of a turntable, and so brought in succession before the diamond and the cracking-off flame. The holders themselves rotate

on central vertical spindles, and it will be noted that they are shaped to fit the ware, so that with change of ware the holders must also be varied. A 40-flame gas burner is used for heating the edge, and the speed of the table and height of the diamond and flames allow of simple adjustment.

For large or thick-walled articles a cutting tool is employed. It consists of a wedge-shaped wheel mounted at the end of a horizontal spindle and driven through a belt from the main power shaft. The object is held firmly against the edge of the wheel and successive cuts are made along the line of severance until by a slight pressure the cap can be removed.

(392) **Smoothing the Edge.**—Cracking-off leaves a rough edge, and as a finishing process this must be smoothed. Two methods are available: if the ware is thick-walled it is ground and polished; if the walls are thin the required result is obtained by heating the edge until it just melts. Machines for both these processes will now be briefly described.

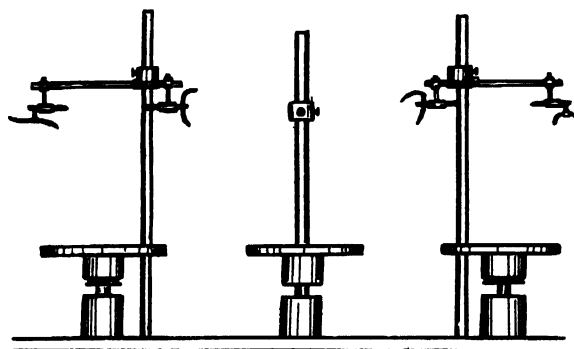


FIG. 247.—A CRACKING-OFF MACHINE.

Grinding is performed by means of a grindstone. The glass is fixed into a wooden chuck at the end of a horizontal spindle, so that the edge to be smoothed lies in a vertical plane. A grindstone with a flat vertical face, fixed on to a second spindle in line with the first, can be pressed against the rough edge of the glass by a lever, the pressure being maintained in grinding by a spring. A pulley drive serves to keep the chuck and glass in rotation during grinding, whilst the stone is kept moist by the continual dripping of water upon it. Since, by wear, a circular ring is worn upon the stone, this latter can only be used for articles of exactly the same diameter, or fracture of the glass will result. After grinding, polishing is performed in a similar manner by means of a wooden wheel. In many works the glass is held by hand against the grinding wheel.

(393) **Melting the Edge.**—Several types of machine exist for the purpose of smoothing the edges of thin-walled ware by melting, and their action may be summarised as follows. A ring or endless chain, rotating in a horizontal plane, carries a series of small circular tables, each of which also rotates on a central vertical spindle. Upon these

tables, in succession, are placed the articles to be smoothed. They are thus carried by the conveyer through a metal tunnel surrounding the upper portion of the glass. The first portion of this tunnel serves to preheat the edges, either by means of broad flames or by hot waste gases from the softening flames lying further back. When sufficiently heated the glassware passes through a zone where flames play directly upon the

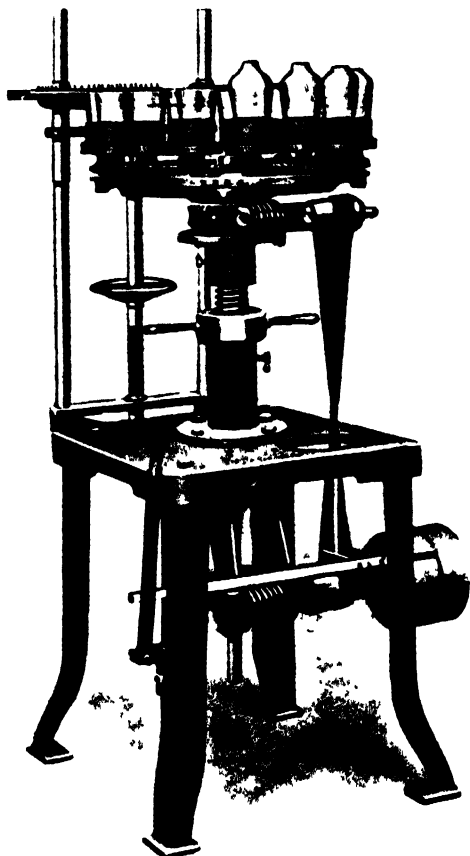


FIG. 248.—AN AUTOMATIC CRACKING-OFF MACHINE.
(By courtesy of Messrs. C. Melin and Co, London.)

edges until these are softened and so become smoothed. On emerging from the tunnel the glasses are removed by means of wooden tongs and replaced by fresh articles. Fig. 249 illustrates a machine of this kind manufactured by Messrs. C. Melin and Co.

(394) **Glass Cutting.**—Cutting is a mode of decorating glass brought out in modern times, and there is no record or example of ancient glass

which is treated or shaped in the manner of modern cutting. It is based on the principle of geometric combinations of incised grooves sunk in the surface of the glass and then brought up to a high polish. A glistening and brilliant effect is thus obtained by the light being refracted from the facets and angles which form the pattern.

In good cut patterns the article to be cut is first accurately divided, by some form of good adhesive ink, into the required number of points, which will be the guide to run intersecting lines through, and which go

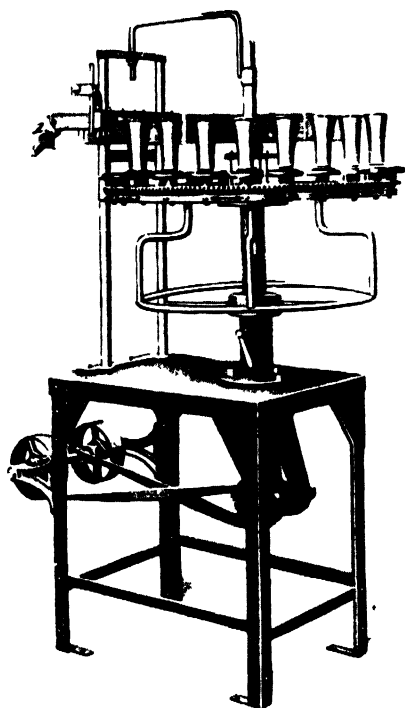


FIG. 249.—A REMELTING MACHINE.

(By courtesy of Messrs. C. Melin and Co., London.)

to form the geometric basis of the design. This dividing in large establishments is frequently done by women, and is called "marking."

Good patterns of a necessary depth in the glass to obtain the best effect, are subjected to a first process which is called "roughing in." An iron or soft steel mill or disc fixed on a horizontal spindle runs in a frame standing in front of the workman. Over the top edge of the revolving mill is slung a large hopper containing good sharp sand of the white variety, mixed with water. This mixture is allowed to run in a thin stream on to the top of the mill edge in front of the article, which is held on the *top* edge of the mill by the artisan. By the abrasive action of

the sand between the surface of the mill and the surface of the glass, the latter, being of a softer nature, is naturally cut away and the depth and rough formation of the design is obtained.

The article is then passed on to another workman, whose process is called the "smoothing in" of the pattern—*i.e.*, following the lines made by the "rougher" but elaborating them by deepening, widening, and very often adding to the design finer lines. This process also brings the cuts from a rough appearance left by the sand to a smooth surface. The workman works on a *stone* which is mounted similarly to the mill, but water only is allowed to run on the stone.

When this workman has finished with it the design is complete, but it is in a dull or semi-obsured state.

This has, therefore, to be subjected to a polishing process in order to bring the design out in the original brightness of the body of the article. If of a good pattern, with large and bold cuts, the article is now held on a *wooden* disc, mounted similarly to the mill and stones, on the edge of which is fed fine powdered pumice and water. This puts a semi-polish to the principal cuts of the design.

Next it passes to the "brusher," who has a high-speed hard bristle brush revolving in front of him, also fed with pumice and water. This brushes a semi-bright surface over *all* the lines of the pattern.

The last process of all is the "putty polishing." The putty is a powder composed of lead and tin oxides mixed with water and applied to a high-revolution brush. This puts the final beautiful pristine brightness to the pattern, and allows the facets of the cuts to reflect light in the scintillating rays which is the attraction of good cut glass.

(395) **Engraving on Glass.**—This is a very old art. It is difficult to find the earliest period in which it was used. Evidence of its application is apparent on some of the discovered specimens and fragments of Greco-Roman glass, and probably the Chinese used a crude form of engraving apparatus to assist with their carving of glass.

The modern apparatus comprises a lightly constructed table lathe, with its head stocks and bearings about a foot high from surface of bench, and placed about a foot back from the front edge of the bench, and parallel to it. A mandrel runs through the two bearings, and projects about four inches. The projecting part is hollow, and a large number of spindles are made to fit this hollow mandrel. On these spindles may be fixed various sized copper discs. The sizes used depend on the class of work desired, and vary from one-sixteenth to four inches in diameter. The artisan himself supplies the motive power for the lathe by means of a driving wheel fixed under the table, the crank of which is connected to a treadle and worked with his foot. He regulates the speed by practice according to the work he is on. The copper wheels or discs are fed with emery powder in oil. The article is held up to the disc on the *under* side and moved and twisted about to obtain the desired pattern. This mode of work is specially applicable in obtaining fine and delicate effects of a flowing style of decoration. In fact, with a clever artisan it enables high-class and very artistic results to be obtained.

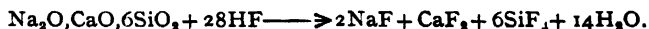
Sometimes the decoration is left dull on the bright body of the glass, or, in a style of engraving known as "rock crystal," where the engraving

is deeper, it is brought back to a high polish with either acid process or the brush.

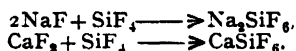
(396) **Intaglio Work.**—Intaglio work is quite a modern invention, originated by the late John Northwood in collaboration with Messrs. Stevens and Williams, Ltd., Brierley Hill, a few years ago.

This is a method of partly engraving and partly cutting. A lathe, which was also invented by Northwood for the purpose, is constructed to work by motive power and to be easily adjusted by the workman to obtain varying speeds. The lathes are mounted on the bench in the same way as the engraving lathes, but on the spindles are stones fixed in place of the copper discs. Water is allowed to run on the top edge of these, and the article is held on the *under* cutting edge of the stones. Bolder work and more decisive style of cuts and decorations can be obtained in far quicker time than in engraving. Larger surfaces can be covered in modelling commercial pieces than would be practical in the smaller process of engraving.

(397) **Etching.**—In our study of the effect of acids upon glass we noted the striking difference between the action of hydrofluoric acid and that of all other acids. With the former the attack is rapid and vigorous, and results in the breaking up of the silicates with the production of gaseous silicon fluoride. In the case of a soda-lime glass the action may be expressed by the following equation:



The fluorides liberated further react to give sodium and calcium silico-fluorides:



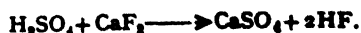
Sodium silico-fluoride is fairly soluble, but calcium, potassium, and lead silico-fluorides are insoluble and remain as a deposit on the surface of the glass. These loose layers of deposited salt prevent free action of the acid, and the surface is attacked unevenly if they are not removed, giving to the glass a frosted or "matt" effect.

Resistance to attack varies with the different types of glass, heavy lead glasses being most readily, and hard potash glasses least readily, attacked by hydrofluoric acid. The following etching processes may be distinguished.

(398) **Deep Etching.**—This may be performed by the action of the gaseous hydrofluoric acid itself, or by a liquid bath consisting of a more or less dilute solution of the acid in water, sometimes reinforced by the presence of other acids—that is, sulphuric acid for lime glasses and nitric acid for lead glasses. The process may be used for producing raised designs, line patterns, or to remove flashed colours from the surface of the glass.

I. **GASEOUS HYDROFLUORIC ACID** is chiefly used for etching line patterns. Articles to be etched are placed on shelves around the sides of a lead-lined wooden box, the lid of which can be sealed by a rubber joint. In the centre of the bottom is a small lead-lined iron boiler or still containing sulphuric acid and calcium fluoride. From the centre of the lid a narrow lead pipe leads to a flue with a strong draught.

The still is heated with a small burner from below until thoroughly hot, the flame is removed and the box left for two days. Hydrofluoric acid is produced by the interaction of the fluorspar and sulphuric acid thus—



After standing, residual fumes are removed by a current of air blown through a small pipe at the bottom of the box.

II. ACID BATHS are obtained as indicated above, and the etching is performed by dipping the glass for a suitable period into the bath. In order to obtain a deep clear etch, precipitated salts must be removed, by either keeping the glass in motion during etching, or else by rubbing the surface from time to time with a brush. With a more dilute acid attack is slower but a brighter result is obtained. Suitable baths for deep etching are:

SODA-LIME GLASS.

I.				II.			
Concentrated acid	hydrofluoric	Concentrated acid	hydrofluoric
Water	1 part	Water	1 part
			4 to 5 parts	Sulphuric acid	3 to 10 parts
							1 part

LEAD GLASS.

Concentrated hydrofluoric acid	1 part.
Water	3 to 10 parts.
Nitric acid	1 part.

Hydrofluoric acid and etching solutions containing this substance can only be kept in suitable vessels, those of lead or gutta-percha being the best. The acid must by no means be allowed to touch the skin, and it must be kept in a fume cupboard, since to inhale the fumes is dangerous. In order to produce a design by etching, portions of the glass surface must be suitably covered with a "*resist*," a thin layer of material capable of adhering to the glass and not attacked by the acid. The simplest form of resist is a layer of wax painted on the glass or laid on in the form of a thin waxed paper. In some cases the surface is covered with a layer of tinfoil in which the design is cut. The following resists are very effective:

For Painting.				For Printing.
	Thin.	Medium.	Viscous.	
Asphalt	500	500	500	500
Resin	200	300	300	100
Tallow	100	—	—	500
Venetian turpentine	200	100	100	300
Turpentine (rect.)	1,200	1,000	800	800
Beeswax	—	150	150	300
Varnish (Tunis)	—	—	—	700

To prepare, carefully melt the solid constituents (they are highly inflammable) and stir in the liquids (turpentine, etc.). Keep in a tightly closed bottle or tin. At above 70° C. the resist peels from the glass surface.

(399) **Matt Etching.**—The deposition of crystals of silico-fluoride on the surface of the glass, and consequent unevenness of the acid attack, though fatal in the case of deep etching, is the secret of successful matt etching. In order that it may be secured, an etching bath containing not only hydrofluoric acid but also a fluoride is used. Since sodium silico-fluoride is fairly soluble, potassium or ammonium fluorides are used, the latter acting strongly and giving a rough matt.

Matt etching may be produced by painting the glass surface or by dipping into a suitable bath. The process takes rather a long time and is apt to give uneven results, although this can be remedied by the presence of a neutral salt in the solution (see Miller's matt bath below). Generally, a somewhat higher temperature than normal is needed (40° to 60° C.), and this, for success, must be kept as constant as possible.

MATT ETCHING SOLUTIONS.

Bath I

Potassium fluoride	10 parts.
Hydrochloric acid	1 part.
Water	100 parts

This bath acts best at 40° to 60° C., a lead vessel being the most suitable container. Hydrofluoric acid is obtained by the action of the hydrochloric acid on the fluoride.

Bath II.

Ammonium fluoride	5 parts.
Hydrofluoric acid	2 „
Water	5 „

This gives a coarse matt, it is rapid at ordinary temperatures, and best put on with a brush. After a few minutes, wash off with water.

Bath III. (Miller's).

Ammonium fluoride	500 parts.
Ammonium sulphate	50 „
Sulphuric acid	100 „
Water	500 „

(400) **Pastes for Stamping.**—(a) A concentrated solution of ammonium fluoride in hydrofluoric acid is poured on to a stamping pad, and after spreading evenly is stamped on to the object with an indiarubber stamp. Etching is complete in a few minutes.

(b) Five parts of ammonium fluoride and one and a half of sulphuric acid are ground with gelatinous silica (obtained by the addition of acid to water glass) and this then used as a stamping compound. A beautiful effect results on standing 24 hours in a warm place.

(401) **Etching Ink.**—Add water slowly to a mixture of 4 grams of ammonium fluoride and 12 grams of precipitated barium sulphate (about

15 grams of water are needed). When required, take 4 grams of the paste with 4 drops of concentrated sulphuric acid.

(402) **Acid Polishing.**—Much decorated glass is now finally polished with hydrofluoric acid, instead of with a wooden polishing wheel. A bath for acid polishing consists of a mixture of strong hydrofluoric acid with strong sulphuric acid, thus—

Hydrofluoric acid (concentrated)	1 part.
Sulphuric acid (concentrated)	2 parts.

The article, after first cleaning in a bath of dilute hydrochloric and sulphuric acids, is immersed for 15 to 45 seconds and then transferred rapidly to a bath of warm water. This process is repeated three or four times and the glass is then dried in a warm place.

Acid polishing is quicker than mechanical polishing, but the finished surface is more liable to attack by weathering agents, and the polish is less permanent. Pressed glass containing barium oxide does not readily acquire an acid polish.

(403) **Etching Machines.**—The so-called etching machines are designed for cutting out a line pattern at the surface of glassware when this has been uniformly coated with wax. They do not actually mark the glass, but merely remove wax, so that, later, the glass may be acted upon by hydrofluoric acid along the lines cut. One very simple form of apparatus cuts regular designs by combining the effects of a rotational movement of the glassware with a reciprocal vertical motion of the graving tool, thus producing a wave effect.

In the "*pentagraph*" any desired pattern is followed by a style, and the motion so given is communicated to a large number of cutting tools, which reproduce faithfully on the glass the motions of the style. It is thus possible to mark at one time a number of separate articles with any desired pattern.

(404) **The Use of the Sand-Blast.**—A rapid method of producing an etched surface upon glass, somewhat similar to the matt-etching of fluorides, is the process of sand-blasting, first successfully employed by B. C. Tilghman in 1870. The process is now widely employed, since it is very rapid in action, but is generally only economical when many articles require treatment. Several types of sand-blasting machines are on the market, and it is only possible to give an outline of the principles underlying these. All processes depend upon the effect of sharp-grained sand impinging upon the glass surface with a considerable velocity, but differences occur in the methods by which the effect is obtained.

(405) **Air-Blast Machines.**—Air is driven by means of a compressor, fan blower, or Roots' blower into a nozzle, into which, through a side tube, sand is also fed. The sand is thus driven with force against the glass surface held above the mouth of the nozzle. Varying air pressures are used, from about 6 inches water pressure up to 2 atmospheres. Fig. 250A illustrates diagrammatically one type of compressed air sand-blast machine. Into the vertical nozzle, 1, is projected the compressed air from the tube, 2, below. This air, moving with high velocity, sucks in other air from the side opening, 3. Surrounding the nozzle is a chamber, 4, with a hopper bottom in which the sand is placed. A small opening, 5,

allows the sand to trickle from this chamber into the opening **3**, from whence it is carried by the inflowing air into the nozzle, and so projected on to the glass held at the opening **6** above. To prevent sand being projected into the air, the covering plate, **7**, is removable, and one with a hole of suitable size in regard to the object to be etched is used. Since in some cases it is not possible entirely to fill this opening, an exhaust tube, **8**, draws away the fine dust and prevents it from passing into the air. After striking the glass the sand again falls to the bottom of chamber **4**, and is ready for further use.

The escape of finely-powdered sand as a dust into the atmosphere constitutes a danger in all sand-blast machines. It may be minimised by using damp sand, whilst in several forms of apparatus the difficulty is surmounted by placing the article to be etched in an enclosed chamber.

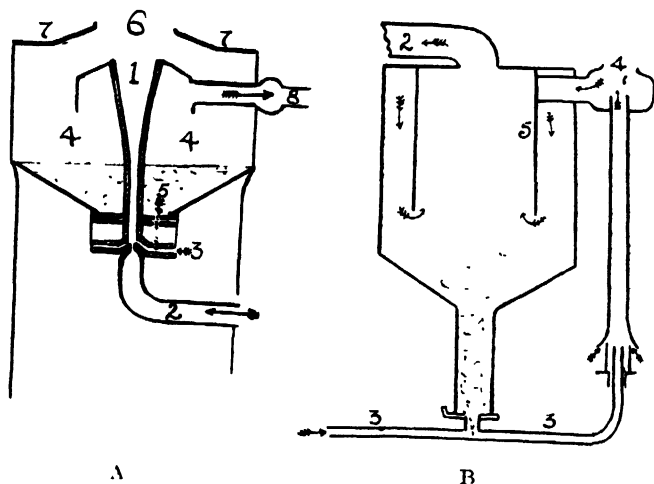


FIG. 250.—SAND-BLAST MACHINES.

In a more modern type of apparatus, due to Mathewson, the sand chamber itself is under pressure, and the sand so forced and not sucked into the blast tube. At the top of the container is a valve only opened from without by the weight of the sand as it gathers in a hopper-shaped receiver. By this contrivance a regular circulation of sand is obtained without loss of pressure in the chamber itself.

(406) **Steam-Blast Machines.**—Steam may be used to replace compressed air, and steam pressures up to six atmospheres are used. The employment of steam tends to endanger glassware through cracking, but this may be prevented by passing a current of air between the nozzle and the glass in a direction at right-angles to the steam jet. By regulating the velocity of this air current steam is carried away without appreciable diminution of the velocity of the sand occurring, whilst by the use of preheated air the sand may be to a large extent freed from moisture.

(407) **Suction Machines.**—The sand in these machines is driven by suction caused by the creation of a partial vacuum in the etching chamber.

One form, due to Mathewson, is shown in Fig. 250B. Sand is contained in a hopper-bottomed vessel, **1**, from which air is sucked through a pipe, **2**, by a suitable fan exhaust. The decreased pressure in **1** causes a rapid inrush of atmospheric air through the bent tube, **3**. Through a small and suitably regulated opening at the bottom of chamber **1**, sand falls into tube **3** and is carried along by the inrushing air. At the elbow **4** is a suitable opening against which the glassware is pressed. Sand travelling along the tube is hurled forward at the bend, and so strikes and etches the glass, being afterwards carried back into the chamber **1**, when it strikes the baffle **5** and falls again into the hopper. Fine dust is prevented from being sucked into the fan by a vessel for water washing the outgoing air, situated between the chamber **1** and the exhaust.

Vacuum machines with enclosed chambers are also made, whilst in some forms of apparatus the pressure and suction effects are combined.

(408) **Centrifugal Machines.**—Sand falls into buckets situated at the circumference of a rapidly rotating wheel, and is from thence hurled on to the glass surface with sufficient force to etch the material.

(409) **The Morse Gravity Machine.**—Sand, mixed with some harder material, such as carborundum or emery, falls from a hopper down a tube eight feet long on to the surface of the glass. Sand alone would not be effective, and the abrading mixture is made up according to the hardness of the glass to be treated. Accumulation of sand on the glass is prevented by continuously sweeping it from the surface into a suitable receptacle. The Morse apparatus has the advantage of being economical when only a few articles have to be treated.

(410) **Stencils and Resists.**—In order to produce etched designs by sand-blasting, stencils are largely employed to protect portions of the glass. As a material for preparing stencils zinc foil is found to be very successful. Designs may be cut from this by means of a sharp knife or graving tool, but more complex patterns are better made by painting the parts of the metal not to be removed with a resist, such as is used in acid etching, and dissolving away the unprotected portions by means of dilute nitric acid. Printed designs may be transferred to the stencils by means of suitably prepared metal printing plates.

Instead of metal stencils indiarubber preparations are found very effective for coating the glass. These compositions are painted or squeegeed on through a stencil and allowed to stand for half an hour, after which time the glass may be subjected to the action of the blast.

A composition may be made by finely cutting up indiarubber and dissolving it in benzene by allowing the two to stand together a day in a well-stoppered bottle. This rubber solution is then mixed with soot and applied to the surface of the glass. A resist useful for printing on the glass by means of an etched steel plate is the following: liquid glue, 25 parts by weight, glycerine 15, whiting 70.

(411) **Iridescent Glass.**—Beautiful colour effects are obtained in a very simple manner by exposing the surface of hot glass for a short time to the action of metallic salt vapours. By this means an extremely thin layer of glass on the surface of the material is subjected to chemical change. Light, falling on the surface, is partly destroyed, certain colours of the incident white ray being lost, due to a phenomenon known as

interference. The reflected ray is complementary in colour to the colour destroyed, and the colour actually obtained depends upon the thickness of the attacked layer on the surface of the glass. This varies over the article, and as a result, no one colour is obtained, but the glass is given a delightful iridescent appearance. Most successful of all salts used for this purpose is stannous chloride (SnCl_2), and this is uniformly employed, though other salts are added for the production of special effects. The following are typical mixtures used:

- (1) *For ordinary effects*—pure stannous chloride.
- (2) *Blue shades*—stannous chloride 80 parts, strontium nitrate 5 barium chloride 15.
- (3) *Red shades*—stannous chloride 88, strontium nitrate 7, barium chloride 5.
- (4) *Opalescent effects*—stannous chloride 90, bismuth nitrate 10.

The surface of the glass must be perfectly clean, and the results obtained depend upon the temperature and the time of action. In use, a special muffle furnace is employed with a deep vertical recess open

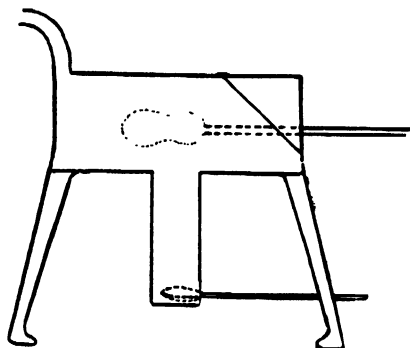


FIG. 251.—A MUFFLE FURNACE FOR PRODUCING IRIDESCENT GLASS.

near to the bottom (Fig. 251). Whilst the article of glassware is in the process of manufacture, that is, just before it is cracked off from the pipe or punty, it is heated to the required temperature (a red heat) at the working hole, and then held in the closed chamber of the muffle. Meanwhile an iron ladle has been heated, and into this is dropped the powder for producing iridescence, which is then thrust into the recess below the muffle. The heated salts vaporise and pass into the upper chamber, where attack takes place, finally passing away to the chimney. Variations of this method give the well-known ware on the market, such as "Favrile" glass, "mother-of-pearl" glass, etc. The best glasses to use for this purpose are crystal or fairly dark-coloured glasses.

(412) "**Lustring**" of Glass.—A solution of a metallic resinate is made in an ethereal oil, such as lavender, rosemary, or light camphor oil. The article to be treated is dipped into this, or is painted over with a brush, dried, and heated, when a beautiful lustrous effect is produced.

The resinate may be obtained by adding metallic nitrates in correct amount to molten resin. A second mode of preparation is by mixing

solutions of metallic salts with sodium resinate (obtained by boiling resin with a caustic soda solution), in which case the insoluble resinate is filtered off, dried, fused, and dissolved in oil. As examples of lustring solutions we may give:

(1) Iron resinate 1 part, lead resinate 1, oil 2—reddish-brown effect.

(2) Cobalt resinate 1, lead resinate 1, oil 2—grey lustre.

(3) Manganese resinate 1, lead resinate 1, oil 2—brownish lustre.

(413) **Enamelling.**—Two methods are in use for decorating the surface of glassware with colour. One is a cold process in which the colours are merely painted upon the glass surface with a brush and then quickly dried. Such designs may be easily scratched from the glass. In the second process designs are painted on as before, but after drying the glass is placed in a muffle furnace and brought for a short time to a red heat. Colours so burnt in are metallic oxides or salts, or in some cases the metals themselves, together with a suitable flux, such as is got by fusing a mixture of sand, red lead, and borax. As a medium for applying the powdered enamel a good varnish or lacquer is necessary. When the colouring medium is heated in the muffle it melts to form a true glaze on the surface of the glass. The following are some of the chief colouring agents used:

YELLOW: Barium chromate, lead chromate, uranium compounds, Naples yellow (an antimony-lead compound).

RED: Ferric oxide, chrome red (basic lead chromate).

BROWN: Ferric oxide, with zinc, nickel, and cobalt oxides as toning agents.

BLUE: Cobalt oxide, toned by the oxides of aluminium, zinc, or chromium.

BLACK: Cobalt oxide with ferric oxide, manganese dioxide, etc.

GREEN: Chromic oxide (with aluminium, cobalt, or iron oxides for toning), copper oxide with potassium bichromate.

WHITE: Stannic oxide, zirconium oxide, or finely-ground porcelain.

The enamels may be of two classes, opaque colouring enamels or transparent enamels. For the opaque enamels suitable fluxes are: (1) Sand 30 parts, red lead 80 parts; or (2) sand 40 parts, red lead 70 parts, borax 20 parts. For red, brown, and light blue colours the flux is generally first melted, cooled by pouring into water, and finely ground, and then mixed with the colouring agent in the proportion of about thirty of flux to one of colour. In some cases the colouring agent is melted first with the flux, and the enamel then ground and applied. Examples of this class are:

GREEN: 30 sand, 80 red lead, 2 copper oxide, 0.2 potassium bichromate.

DARK BLUE: 30 sand, 80 red lead, 1 cobalt oxide.

BLACK: 30 sand, 80 red lead, 4 cobalt oxide, 2 copper oxide, 1 ferric oxide, 1 manganese dioxide.

For **TRANSPARENT ENAMELS** a suitable flux is 10 parts sand, 70 parts red lead, 20 parts boric acid, or for **PURPLE** colours 10 sand, 80 red lead, 40 borax. Characteristic transparent enamels previously melted together are:

RED: 10 sand, 70 red lead, 20 boric acid, 8 pyrolusite.

YELLOWISH-GREEN: 10 sand, 70 red lead, 20 boric acid, 4 copper oxide, 2 uranium oxide.

MEDIUM BLUE: 10 sand, 70 red lead, 20 boric acid, 2 cobalt oxide.

Other examples in which the flux is first made and then mixed with the colouring agent before applying to the glass are:

GREEN: 100 flux, 8 copper oxide.

SKY BLUE: 100 flux, 1.5 cobalt oxide, 9 aluminium hydroxide (with addition of some chromic oxide when a green shade is desired).

For **METALLIC SILVER EFFECTS** finely divided silver (8 to 10 parts), and lead borate (1 part) are used, with, in some cases, addition of a small amount of basic bismuth nitrate. Silver carbonate may be employed in place of metallic silver. **GILDING** is performed similarly with a suitable gold preparation.

The so-called "*yellow etch*" consists of a finely divided silver compound, such as the chloride mixed thoroughly with yellow ochre. The etch is painted on the glass surface and burnt in, in a muffle furnace, when a yellow colouration of the glass is obtained. Gold and copper compounds may be similarly employed. In the case of copper, the oxide or sulphate is employed, and several firings used, the last being under reducing conditions, when a red etch is obtained.

VIGNETTING is usually done by first covering the glass to be decorated with a coat of dilute water-glass solution applied by means of a rubber stamp. Bronze powder, aluminium or agate is then dusted over, adheres to the glass, and is burnt in, giving a bronze, silvery or white effect respectively.

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